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CXXIX. *The Structure of Light.* *By* Sir J. J. Thomson, *O.M., F.R.S.**

IN the Philosophical Magazine for October 1924 I gave a sketch of a theory of the Structure of Light; the object of this paper is to expand and illustrate that theory and to discuss some effects of the interaction between electrons and light which seem to be characteristic of the theory.

On this theory Light has a two-fold structure: one part of it consists of waves of the same character as those postulated in the Electromagnetic Theory of Light. These waves may be regarded as a periodic distribution of closed lines of electric force similar to those represented in diagrams of the lines of force around a Hertz oscillator. Each portion of a line of force travels at right angles to itself with the velocity of light. If we follow the movement of any one of these lines, we see that since it has a velocity in its own plane it must expand as it travels through space and the density of the energy associated with it get smaller and smaller. We call this assemblage of closed lines of electric force Maxwellian waves of light, or more shortly light-waves.

The other part of the structure of light is of a corpuscular character: the corpuscles are also closed lines of electric force and so will travel through space with the velocity of light, but the lines of force in the corpuscles are so arranged that they travel through space without change of shape,

* Communicated by the Author.

size, or energy. The size of the corpuscles depends upon the frequency of the light, the circumference of the corpuscle being equal to the wave-length of the light; thus for Röntgen rays the corpuscles are of atomic dimensions, for visible light they are much larger than the atoms. For light whose wave-length is not greater than that of visible light, by far the greater part of the energy of the light is in the corpuscles. We shall call these particles light-rays. On the theory we are discussing there is a very intimate connexion between the rays and the waves, the two constituents of light. The rays, like the waves, are supposed to consist of lines of electric force moving at right angles to their direction; the rays are supposed to be systems capable of vibration, the time of vibration of the rays being the same as that of the waves. Though the waves are not supposed to give to or take from the rays any energy, yet it is the waves which determine the path of the rays as the rays have always to travel in the direction of the Poynting vector of the waves.

The rays on this theory consist of rings formed of closed lines of electric force, each line of force being a circle with its plane parallel to that of the ring and its centre on the axis of the ring. The thickness of the ring (measured at right angles to its plane) being small compared with its dimensions in that plane. Each line of force in the ring moves in accordance with the principles of electromagnetism at right angles to the plane of the ring; thus it has no radial velocity, and so the shape and size of the ring and the energy associated with it remain unaltered as it travels through spaces. The ring can vibrate about its circular form, the time of vibration being the time light takes to travel over the circumference of the ring. The ring is in tune with the waves, so that the circumference of the ring is equal to the wave-length of the light. The rings on this theory are the quanta of light, so that Röntgen rays are supposed to have much smaller quanta than those of visible light. These rings possess the most striking properties of the quantum, for—

1. Since they consist of closed lines of electric force, they must, from the electromagnetic theory, travel with the speed of light; this explains why all quanta, whatever may be their energy, travel with the same velocity.
2. Since the rings are closed, their electric fields will be confined to the inside of the ring; thus (with the exception of a case to be considered later) they will not

give up energy to atoms or electrons near which they pass. Again, the mass of the quantum is its energy divided by the square of the velocity of light, the energy is hn, where h is Planck's constant $6{\cdot}55 \times 10^{-27}$ and n the frequency of the light. It follows from this that unless the frequency of the light is as great as that of very hard γ-rays, the mass of the quantum will be exceedingly small compared with that of an electron; hence a collision between a quantum and an electron can only give rise to the transference of a very small fraction of the energy of the quantum to the electron. To transfer the bulk of the energy in the ring forming the quantum to an electron a radical change is necessary—the ring must break, its lines of force must cease to be closed and become part of a tube of force connecting an electron with a positive charge, in some such way as that described in the former paper. The energy in the ring will be thrown into the circuit connecting the electron and positive charge and will be available for dragging them apart. If the energy is sufficient to drag the electron to an infinite distance or to a place where it is in stable equilibrium, the ring will be permanently destroyed and its energy transferred to the electron. If the energy is not sufficient for this, the electron, after being dragged some way from the atom, will, under the action of the restoring force exerted upon it by the atom, retrace its path, the ring will be reformed, and there will be no absorption of energy. Thus the energy of the quantum is transferred wholly or not at all, and for each quantum absorbed a high-speed electron is liberated. Thus, when a given number of quanta are absorbed in a gas, the same number of high-speed electrons will be produced whatever may be the nature of the gas—this result was obtained long ago by Barkla.

3. If the rings forming the quanta for different kinds of light are geometrically similar to each other, *i. e.* differ in size but not in shape, the energy in the quantum will be inversely proportional to the circumference of the ring (Phil. Mag. [6] xlviii, p. 737). As the circumference of the ring is equal to the wave-length of the light, the energy in the ring will be directly proportional to the frequency of the light.

The ring of lines of electric force forming the quantum produces a strong electric force inside the ring but no force

outside, the electric force is thus discontinuous at the surface, and the surface of the quantum is thus a surface of discontinuity in the electric field. The problem of the propagation of surfaces of this kind has been discussed by Love in his paper on "Wave Motions with Discontinuities at Wave Fronts," Proceedings London Mathematical Society, series 2, vol. i, p. 37, 1903. He shows that the conditions for propagation of a surface of discontinuity are

α. That the surface travels at right angles to itself with the velocity of light.

β. The electric and magnetic forces must be tangential to the surface of discontinuity.

The electric and magnetic forces due to the ring itself, if it is a thin annulus, will satisfy these conditions. Hence, when the ring is surrounded by the field of electric and magnetic forces due to the Maxwellian waves, the electric and magnetic forces in these waves must also be tangential to the surface of the ring, *i. e.* the normal to the surface, which is the direction along which the ring moves, must be at right angles to the electric and magnetic forces in the Maxwellian waves. Since the Poynting vector of these waves is at right angles to the electric and magnetic forces, it follows that the ring must travel along the Poynting vector. Thus, on this theory, the Maxwellian waves act as guides to quanta of the same period ; when such quanta are surrounded by the waves, they are constrained to travel along the Poynting vectors of the waves. The waves do not give up any energy to the quanta or take any away from them. Thus the effect they produce does not depend upon any definite amount of energy being available from the waves, and though the momenta of the quanta as, for example, in reflexion, refraction, and diffraction may change, yet all these phenomena involve the presence of matter, and this can receive the momentum lost by the quanta.

It is not necessary to suppose that one set of Maxwellian waves can guide only one quantum—we should expect it to be able to control any quantum of the right period liberated whilst the wave was passing over the place of origin of the quantum.

The polarization of light on this view arises from the polarization of the Maxwellian waves and not to any change in the quanta.

Relation between the Energy in the Quantum and that of the Maxwellian Waves.

The measurement of the amount of energy in the Maxwellian waves is beset with great experimental difficulties. The energy in these waves is spread throughout a large volume, and the amount (except in cases of resonance) which could be given to an individual electron or molecule would be exceedingly small; *e.g.*, the energy given to an electron by the waves themselves is of the order of the energy contained in a volume of the wave equal to $\lambda^2 d$, where λ is the wave-length, d the radius of an electron. Thus we could not expect these waves to produce any effect when the intensity of the light is measured by ionization, by photo-electric effects, or by chemical changes—a calorific effect is about the only one they could produce. If the energy in the Maxwellian waves is appreciable, the heat produced when light containing N quanta of frequency n are completely absorbed will be greater than Nhn. Again, if we look at the question from another point of view and consider the energy required to excite light of a definite wave-length, the evidence as to the amount of energy in the Maxwellian waves is ambiguous. Thus, when there is resonance radiation, as, for example, when sodium light is absorbed by sodium vapour, the resonance light has the same energy in the quantum as the incident light; thus, if a quantum of the incident light had to find the energy for the quantum of the resonant light, and for its Maxwellian waves as well, the energy in the latter must be negligible. There are, however, other sources from which the energy of the Maxwellian waves might be derived. The energy in the Maxwellian waves of the incident light is available, and again there are not so many quanta emitted as absorbed; some of the energy of the incident light appears as an increase in the temperature of the absorbing vapour, and in the transformation from the energy in the quanta to the energy of translation of the molecules of the vapour some energy may be spent in exciting Maxwellian waves.

As the density of the energy in the Maxwellian waves diminishes as the waves recede from their source, while the energy in the quantum is invariable, there can be no fixed relation between the energy in the quantum and the density of the energy in the Maxwellian waves. Again, one set of these waves may, as we remarked before, guide more than one quantum; where this is the case, the optical effects will be the same as if these quanta started from the origin of the

Maxwellian waves and not from the places where the quanta were liberated.

There is, however, one case at any rate where the energy of the Maxwellian waves must come from the energy of the quantum: this is when there is the change discovered by Compton in the frequency of Röntgen rays when their quanta give up a little of their energy to electrons; here, since there is a change in the wave-length, there must be a change in the Maxwellian waves and new ones will have to be produced by the quantum. Thus the change in the energy of the quantum would be equal to the energy communicated to the electron plus the energy required for the Maxwellian waves. Thus from measurements of the change of frequency corresponding to the deflexion of the rays through a known angle we might get data for determining the energy in the Maxwellian waves.

The relative amounts of energy in the quanta and that spent in producing Maxwellian waves would from our point of view depend to a large extent on the character of the waves; there must be certain features attending the production of the light to cause quanta to be emitted at all. There does not from this point of view seem any reason for supposing them to exist in long waves such as those used for wireless telegraphy, which have frequencies very small compared with any known frequencies associated with atoms or molecules, and which might conceivably be generated by moving a magnet to and fro. In waves of this kind we should expect all the energy to be in the Maxwellian waves and the quanta to be absent, while in waves at the opposite end of the scale, such as Röntgen rays, we should expect the greater part of the energy to be in the quanta.

Method of Production of Quanta.

Let us take as a typical example the production of radiation by the falling in of an electron E towards a positive charge P. We suppose that the electrostatic potential energy when the charges are at P and E is located in the space round PE and is bound up with the lines of force stretching between P and E. If the electron acquires kinetic energy by approaching P, energy that was previously distributed between P and E must have moved close up to E and be concentrated round it in a volume comparable with the volume of the electron. This transport of energy requires time, and if the electron were to move

very rapidly from E to another point E′ there might not be time for the energy in the outlying field to move to E′. The result would be that the region would be surcharged with energy, and the excess of energy would have to escape; one way of escape would be for it to be radiated as a quantum of light, or, if there were any free electrons in the region, some of the energy might run into them and increase their kinetic energy. If this effect took place simultaneously with the emission of radiation, the frequency of the quanta emitted would diminish as the energy given to the electrons increased. The various quanta would produce a continuous spectrum with a bright edge on the high-frequency side, at a frequency corresponding to the conversion of all the excess energy into radiation.

We may visualize the production of the quantum by supposing that owing to the rapid motion of the electron the tube of force connecting it to the positive charge is thrown into a loop, and that the loop, forming as it does a closed line of force, breaks away and travels out as the quantum.

As the circumference of the quantum is equal to the wave-length of the light, and as for Röntgen rays the wave-length is of atomic dimension while for visible light the wave-length is much greater, it follows that for Röntgen rays the energy of the quantum is concentrated into a volume comparable with that of the atom, while for visible light the energy in a volume of the quantum equal to that of the atom is but a small fraction of the whole energy. This difference in the sizes of the quanta accounts for the very conspicuous difference between the absorption bands for visible light and for Röntgen rays. The absorption bands for visible light are often exceedingly sharp; the absorption seems to be practically entirely confined to the light, with frequencies between very narrow limits. For Röntgen rays, however, though the absorption begins quite abruptly at a particular frequency, light of a higher frequency is also absorbed to an appreciable extent, so that there is a wide absorption range with a well-defined edge on the low-frequency side. This is what we should expect from the view we have taken of absorption, which requires that if the energy given to the electron exceeds that corresponding to the ionizing potential absorption may take place. In this case the absorption is not dependent upon resonance; in the case of ultra-violet light, however, it is. Let us consider what resonance does. Dr. Horace Lamb and the late Lord Rayleigh have shown that when resonance is sharp the

amount of energy streaming into the resonator is not measured by the cross-section of the resonator, but that all the energy from an area of the wave-front equal to λ^2/π, where λ is the wave-length, is focussed on the resonator. Poynting vectors starting from anywhere in this area all pass through the resonator.

Thus when, as in the case of Röntgen rays, the dimensions of the resonator are comparable with the wave-length of the radiation resonance will not materially increase the amount of energy it receives. The conditions are entirely different with visible light, for here the wave-length is very much greater than the dimensions of the resonator. So that resonance produces an enormous concentration of the energy reaching the atom. The energy in the quantum whose area is proportional to λ^2 is by resonance concentrated into the bulk of the atom.

Effects due to Collisions between the Quanta and Electrons.

On the theory we are discussing, there are strong electric forces inside the quantum. Thus the passage of the quantum over an electron at rest may be expected to result in the increase in the energy of the electron at the expense of that in the quantum; the loss of energy by the quantum would reduce the frequency of the light.

Let us suppose the quantum to be a ring whose thickness measured at right angles to its plane is a, and that the difference between the external and internal radii of the ring is b. If the quantum overtakes a free electron at rest, the electron will be inside the quantum for the time a/c, where c is the velocity of light.

If F is the electric force in the quantum, v the velocity communicated by it to the electron, e the charge on the electron, and m its mass,

$$mv = \mathrm{F}e\frac{a}{c}. \quad \ldots\ldots \quad (1)$$

The product of the electric force into the cross-section of the ring is constant; hence

$$\mathrm{F}ab = 4\pi se, \quad \ldots\ldots \quad (2)$$

where s is a fraction and e the charge on an electron.

Both a and b are proportional to λ; let $a=k\lambda$, $b=k_1\lambda$, λ being the wave-length,

$$\mathrm{F}kk_1\lambda^2 = 4\pi se, \quad \ldots\ldots \quad (3)$$

E, the energy in the ring, is equal to $F^2/4\pi$ times the volume of the ring; hence

$$E = \frac{F^2}{4\pi} kk_1\lambda^3 = \frac{4\pi s^2e^2}{kk_1\lambda} = \frac{4\pi s^2e^2n}{kk_1c},$$

where n is the frequency of the light. Thus

$$h = \frac{4\pi s^2e^2}{kk_1c},$$

h being Planck's constant.

Substituting the value of F given by equation (2) in (1), we have

$$mv = \frac{4\pi se^2}{k_1\lambda c}$$

$$= \left(\frac{4\pi e^2h}{c}\right)^{\frac{1}{2}} \left(\frac{k}{k_1}\right)^{\frac{1}{2}} \frac{1}{\lambda}. \quad . \quad . \quad . \quad . \quad (4)$$

Thus the momentum communicated to the quantum is proportional to the frequency of the quantum. Substituting the numerical values for e, h, c, m, we find

$$v = \cdot 86 \left(\frac{k}{k_1}\right)^{\frac{1}{2}} \frac{1}{\lambda}.$$

k/k_1 will be less than unity, so that the velocity communicated by a quantum of light of wave-length 10^{-8} cm. will be considerably less than 10^8 cm./sec.; the energy corresponding to this velocity will be less than that represented by a volt, and will only be a small fraction of the energy of the quantum.

The momentum of the quantum is hn/c, while that of the electron is mv; the ratio of the two is equal to

$$\frac{mv \times c}{hn} = \left(\frac{4\pi e^2}{hc}\right)^{\frac{1}{2}} \left(\frac{k}{k_1}\right)^{\frac{1}{2}}$$

$$= 1 \cdot 2 \left(\frac{k}{k_1}\right)^{\frac{1}{2}} \times 10^{-1}, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and is constant.

The energy acquired by the electron and lost by the quantum is $mv^2/2$: this by (4) is equal to

$$\frac{4\pi e^2h}{2mc} \frac{k}{k_1} \frac{1}{\lambda^2}.$$

If δn is the change in the frequency of the quantum, $h\delta n$ is equal to the change in energy. Hence

$$\delta n = -\frac{2\pi e^2}{mc} \frac{k}{k_1} \frac{1}{\lambda^2}.$$

But

$$\delta n = -\frac{c\delta\lambda}{\lambda^2}.$$

Hence

$$\delta\lambda = \frac{2\pi e^2}{mc^2}\frac{k}{k_1}$$
$$= 1{\cdot}7\times10^{-12}\frac{k}{k_1}. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This is the increase in wave-length a quantum would experience if it passed over a free electron at rest. The area of the surface of the quantum is $k_1\lambda^2$. If N is the number of free electrons per c.c. in the region through which the quantum is passing, the number of electrons a quantum will pass over in a distance δn is $k_1\lambda^2 N\delta x$. Hence from the preceding expression we get

$$\frac{d\lambda}{dx} = \frac{2\pi e^2}{mc^2}k\lambda^2 N$$
$$= 1{\cdot}7\times10^{-12}k\lambda^2 N \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and

$$\frac{dn}{dx} = -\frac{2\pi e^2}{mc}kN$$
$$= 5{\cdot}1\times10^{-2}kN. \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Thus on this view the wave-length of the radiation would increase slowly as the radiation passed through a medium containing free electrons. Compton has shown that when Röntgen rays are scattered the wave-length is increased, but I am not aware of any experiments which show an increase in wave-length due to the passage of the radiation through an absorbing substance.

Scattering of Quanta by Electrons at rest.

We have seen (equation (4)) that the momentum given to an electron at rest by a quantum passing over it is proportional to the momentum of the quantum and is at right angles to this momentum. Thus the quantum will be deflected by the collision through an angle α, where by equation (5)

$$\alpha = \left(\frac{4\pi e^2}{hc}\right)^{\frac{1}{2}}\left(\frac{k}{k_1}\right)^{\frac{1}{2}} = 1{\cdot}2\left(\frac{k}{k_1}\right)^{\frac{1}{2}}\times10^{-1}.$$

This angle is constant if, as we have supposed, F the electric force in the quantum is constant. If this force depends on the distance from the centre of the quantum,

then the angle through which the quantum is deflected by collision with an electron will depend upon the part of the quantum ring struck by the electron.

Multiple Collisions.

The direction of the deflected particle may be any generator of a cone whose axis is the undeflected direction and whose semi-vertical angle is α. Hence, by the theory of probability, after a quantum has made a large number p of collisions, the probability that it has been deflected through an angle between θ and $\theta+\delta\theta$ is

$$\frac{2}{p\alpha^2}\epsilon^{-\frac{\theta^2}{p\alpha^2}}\theta\,.\,d\theta.$$

If ϕ^2 is the mean value of θ^2,

$$\phi^2 = p\alpha^2.$$

If the quantum has made p collisions, the change in wave-length is by (6) given by the equation

$$\delta\lambda = \frac{2\pi e^2}{mc^2}\frac{k}{k_1}p$$

$$= \tfrac{1}{2}p\alpha^2\frac{h}{mc} = \tfrac{1}{2}\phi^2\frac{h}{mc} = 1{\cdot}2\times10^{-10}\phi^2.$$

The scattering we are considering arises from the superposition of a large number of minute deflexions. This must be distinguished from the normal scattering to which attention has usually been confined; the intensity of this normal scattering in the simplest cases varies as $1+\cos^2\theta$, so that large angles of scattering are not very much less probable than small ones. This normal scattering is due, not as in our case to the addition of a very large number of small deflexions, but to the production under certain circumstances of one—it may be a large—deflexion of the quantum. The origin of these large deflexions, produced by atoms or molecules in the path of the primary beam, is due to the secondary electrical waves started by the electrons in the atom under the action of the primary, producing in the neighbourhood of the atom electric waves, where the Poynting vector makes large angles with its direction in the primary beam. Thus there is a finite chance that a quantum following the Poynting vector may be deflected through a large angle. If it is deflected its momentum is changed and the change in

momentum must be communicated to the atom, or to the electrons in it. If the momentum is communicated to an electron, the electron will absorb a finite amount of energy and the quantum will lose energy and correspond to a longer wave-length. If the momentum is communicated to the positive core of the atom rather than to an electron, very little energy will be given to the core in consequence of its large mass, and there will not be an appreciable change in the frequency of the quantum. Thus the rays which are scattered by "single" scattering may or may not show a change of frequency. In Compton's experiments the scattering was the normal scattering, and he found part of the scattered light showed a change in frequency and part did not.

The amount of multiple scattering in a direction making an angle θ with the direction of the incident light due to the collisions between the quanta and the electrons and showing a change of wave-length is proportional to $\epsilon^{-\frac{\theta^2}{p\alpha^2}}\theta$, while the normal scattering to $1+\cos^2\theta$. Thus, unless $\sqrt{p\alpha}$ is a large angle, the intensity of the scattered light with smaller wave-length will fall away very rapidly as θ increases and very little of this light will be scattered backwards, while the normal scattering is as great in the rear as in front; hence the best place to look for the light of altered wave-length would be in a direction making a small angle with the incident light.

We have in the preceding calculations supposed that the electron could be treated as free; if the electron forms a part of an atom, the results will only apply when the time taken for the quantum to pass over the electron is short compared with the time of vibration of the electron.

Since all the dimensions of the quantum are proportional to the wave-length, the time taken for a quantum to pass over an electron will be inversely proportional to the frequency; hence electrons which behave as if they were free when acted on by quanta of high frequency, such as those of Röntgen rays, need not do so for quanta of visible light, which have much smaller frequency.

The effect produced by collisions on the frequency of a quantum depends essentially on the size of the quantum; it will vanish when the quantum is large compared with the molecule against which it strikes. For if, as in the case of visible or ultra-violet light, the quantum is very large compared with the molecule, it will envelope the whole of the

molecule, the positive core as well as the electrons. Thus as the molecule is an electrically neutral system it will not gain any momentum from the electrical forces in the quantum ; thus no energy will be given to the molecule and none taken from the quantum, so that no change of frequency will be produced by the collision. This is in accordance with experience, for though changes in frequency have been observed with Röntgen rays whose wave-length is less than 10^{-8} cm., and whose quanta are therefore smaller than the atoms or molecules against which they strike, no such changes have been observed with ultra-violet or visible light when the wave-lengths are hundreds or thousands of times greater than the diameter of the atoms, and the quanta therefore vastly greater than the atoms.

Though the collision of a quantum with a free positive particle would result in the particle gaining as much momentum as an electron, and therefore deflecting the quantum through the same angle, the energy given to the particle and therefore the change of frequency would only be m/M of that for the electron—here m is the mass of an electron, and M that of a positive particle.

The transference of energy between electrons and quanta in the way we have been considering might lead to very important consequences. We can see, for example, that if the free electrons instead of being at rest were in rapid motion, a collision between a quantum and an electron might increase instead of diminishing the frequency of the quantum. Thus, suppose that the electron had a component of its velocity parallel to the plane of the quantum in such a direction that when the quantum passed over it the electric force in the quantum tended to stop the electron.

Then if the initial velocity of the electron is greater than half that which the quantum would communicate to an electron at rest, the electron will lose and the quantum will gain energy, so that the frequency of the quantum will be increased. The greater the velocity of the electron the greater the change in frequency. The passage of quanta of Röntgen rays through a dense swarm of high-speed electrons would, even if the rays were homogeneous to begin with, cause their frequencies at the end to spread over a finite range and thus seriously modify the character of the radiation. One way of producing high-speed free electrons is by means of hard Röntgen radiation, so that a very intense beam of hard Röntgen radiation might affect the average velocity of the free electrons in the medium through which it was passing, and

thereby the character of a beam of soft radiation passing through the medium at the same time.

The frequency of the quantum is increased when the electron struck by the quantum is moving in the direction in which the electric force in the quantum tends to stop the electron ; if the electron were moving in the opposite direction the frequency of the quantum would be diminished by the collision. If V is the tangential velocity of the electron in the first case, the increase in frequency is

$$\frac{mv}{h}\left(\mathrm{V}-\frac{v}{2}\right),$$

where v is given by equation (4).

In the second case the diminution in the frequency is

$$mv\left(\mathrm{V}+\frac{v}{2}\right),$$

where V is the tangential velocity.

Since the lines of electric force in the quantum are circular, when a quantum passes over an electron moving tangentially the electric force in one half of the quantum ring will tend to stop the electron and therefore increase the frequency of the quantum, while in the other half it will tend to accelerate the electron and diminish the frequency. As the chance of the electron being at the collision in one half of the ring is the same as its being in the other, the quantum in its journey will sometimes have its frequency increased by collisions and sometimes diminished. Thus, if a number of quanta started with the same frequency, they would, after collision with many electrons, possess frequencies distributed according to the law of probability, the chance of a departure between x and $x+\delta x$ from the original frequency being proportional to $\epsilon^{-\frac{x^2}{n\alpha^2}}\,dx$, where n is the number of collisions and α the change of frequency due to one collision. Thus the spectrum, which before the collisions was a sharp line, will be drawn out into a band, the breadth of the band being proportional to $\sqrt{n}$. Since the increase of frequency due to a tangential velocity V is proportional to $\mathrm{V}-v$, while the diminution is proportional to $\mathrm{V}+v$, the diminution is greater than the increase ; so that besides drawing the line out into a band, the collisions will produce a continuous diminution in the frequency proportional to n.

In the preceding calculations we have supposed, in accordance with the usual classical theory, that the communication of momentum to an electron in an electric field is continuous and that infinitesimally small increments of momentum can occur. Results of the same general character would ensue if the action of the electric field consisted in the discontinuous additions of finite increments of momentum. For suppose that δt is the time taken by the quantum to pass over the electron, and that $\omega\delta t$ is the chance that the electron will receive an increment of momentum in this time, let k be the increment it receives, if it receives any, then $k\omega\,\delta t$ will be the probable increment of momentum in time δt. Thus the constant force F, which on the average will produce the same effect as the discontinuous addition of momentum, is equal to $k\omega$.

Let us consider what the difference between the continuous and discontinuous actions would be; suppose that k, the increment of momentum on the discontinuous view, is greater than $F\,\delta t$. Thus, when a quantum did lose momentum by collision with an electron it would on the discontinuous view lose more than on the continuous one and would be deflected through a greater angle; on the other hand, it might pass over an electron without suffering any deflexion. If the angle of deflexion for an effective collision on the discontinuous view were twice that on the continuous one, the probability that the quantum suffered any deflexion at all would be only 1/2 Thus when a large number of deflexions were combined, in one case the result would be that of combining N/2 deflexions each equal to 2ψ, and in the other N deflexions each equal to ψ.

The characteristic quantity occurring in the distribution law, $\frac{2}{p\alpha^2}\epsilon^{-\frac{\theta^2}{p\alpha^2}}.\theta.d\theta$, is $p\alpha^2$, where p is the number of collisions and α the deflexion at each collision; when p is halved and α doubled, $p\alpha^2$ is doubled; this means that the scattering is more evenly distributed and is not so concentrated along the smaller angles.

If a quantum gives no momentum at one collision but a double quantity at the next, since double momentum corresponds to four-fold energy, the quantum after passing over the same number of electrons would lose twice as much energy and suffer twice the change in frequency as one losing one unit of momentum at each collision.

If the magnitude of the momentum imparted to the electron were such that the moment of momentum is quantized into multiples of h, then

$$kr = nh, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where r is a length proportional to λ, the wave-length of the light.

Since the momentum of the quantum is h/λ, as λ is greater than r, k, the transverse momentum communicated to the electron, will be greater than h/λ, the forward momentum of the quantum; so that the quantum will, if deflected at all, be deflected through a large angle. From equation (9) k varies inversely as λ. Since $k\omega$ is equal to F and F varies as $1/\lambda^2$, ω will vary as $1/\lambda$; the chance that an electron struck by a quantum receives momentum is $\omega a/c$, now a varies as λ, and since ω varies as $1/\lambda$; the chance that an electron when struck by a quantum should receive some momentum is independent of the wave-length of the light corresponding to the quantum.

Summary.

This paper develops further the theory of light sketched by the author in a paper published in the Philosophical Magazine, Oct. 1924. The effects which on this theory would follow from collisions between quanta and electrons are discussed; it is shown that the quanta would be deflected and lose frequency by colliding with electrons. This deflexion would produce a scattering of the light made up of a great number of small deflexions combined according to the Theory of Probability; this scattering is in addition to that which is proportional to $(1+\cos^2\theta)$, which is accounted for by the wave theory. It is shown, too, that when the electrons are in rapid motion the theory indicates that collisions between the quanta and the electrons will produce an *increase* in the frequency of some of the quanta.

CXXX. *On the Discharge of Electricity between Equipotential Plates.* *By* Mason E. Hufford, *Assistant Professor of Physics, Indiana University* *.

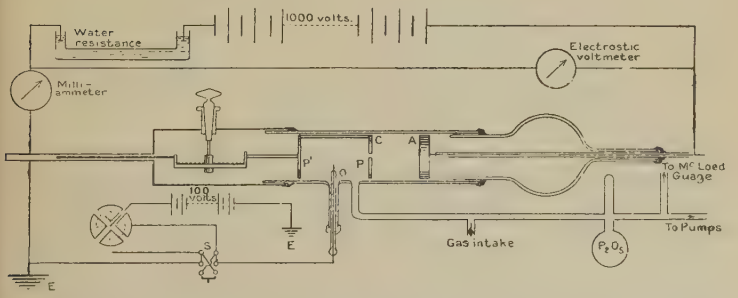
[Plate XXXIV.]

IN a paper † presented to the Royal Institution, Sir J. J. Thomson described conditions under which a beam of canal rays in a low-pressure discharge-tube produces behind the cathode a fully-developed discharge like that between the anode and cathode.

It is the purpose of this paper to discuss the results of a study of the conditions upon which the discharge depends.

For carrying out the experiments essential to these investigations, apparatus was arranged as shown in fig. 1.

Fig. 1.



Here A represents the anode and C the cathode of a discharge-tube. These electrodes were mounted in a glass tube 3 cm. in diameter and were placed 10 cm. apart. The cathode consisted of a front plate P in which a hole had been bored, and a back plate P′. These plates were 4·8 cm. apart and were connected by a heavy metallic conductor.

Plates and conductor were formed from a continuous sheet of metal. The cathode system was joined to a rack and pinion, by means of which the cathode could be moved forward and back in the tube so as to bring the probe O to any desired point between the plates.

The cathode was connected to earth by a heavy metallic conductor.

The probe consisted of a small copper wire shielded by a

* Communicated by Professor Sir J. J. Thomson, O.M., F.R.S.

† 'Proceedings of the Royal Institution,' xix. p. 584 (April 2, 1909).

glass tube of fine bore. The wire projected beyond the end of the tube about a millimetre.

Potentials of the probe were measured by means of a quadrant electrometer whose sensitivity had been adjusted for the purpose. By means of a switch S either pair of quadrants could be connected to the probe and the other pair connected to earth. The needle of the electrometer was connected to the positive terminal of a 40-volt charging battery, the negative terminal of which was earthed. The electrometer was calibrated by means of a Weston current voltmeter, and also by an Ayrton & Mathers electrostatic voltmeter. Voltages were taken from a voltage deflexion curve.

For most of the qualitative work an induction coil equipped with a rotary mercury make and break was used. In the coil circuit a rectifying valve was placed to insure a unidirectional current. For quantitative measurements the coil was replaced by a cabinet of storage-cells yielding a thousand volts. The cell current was regulated by a water resistance.

When voltage is applied to a tube like that described and the pressure has been sufficiently reduced, a discharge begins to pass, first between anode and cathode. As the pressure goes lower and the Crookes's dark space reaches a length of about two millimetres, a very bright bead suddenly passes through the hole in the plate P, and the back surface of the plate gradually becomes covered with a glow. Between the metal surface and the glow is a dark space. As the pressure is further reduced, the entire metal surface is spread over by the glow, and the dark space becomes much wider. Still lower pressure is accompanied by the filling of the whole volume between the plates P and P′ with the glow.

Pl. XXXIV. shows a drawing and a photograph of the fully-developed discharge.

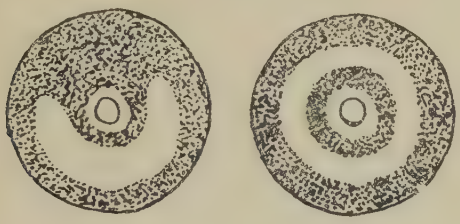
It was found that at a low pressure which depends upon the size of the hole, the material of the cathode, and the gas in the tube, the bead ceases to pass through the hole, the glow disappears and is replaced by a stream of canal rays.

Later experiments in which the plate P could be detached from the cathode and from the earth indicated that under certain conditions of pressure all the metal surface in the system behind the cathode takes part in the discharge.

The presence of the bead and accompanying glow indicate a neutralization of positive rays by electrons evolved from the metal surface. This neutralization is accompanied by a high potential in the glow.

Close observation was made of the beginning of the glow between the plates of the cathode system. When the induction coil was used, it was found that the glow first appears on the back of the cathode P in the form of a crescent. As the pressure is reduced the crescent spreads over the plate surface, leaving an annular ring, not covered by the glow, surrounding the hole. This ring coincides with a band of deposit left on the plate after some hours of use. Quite often the crescent patch of glow was seen to rotate about the opening. In 90 per cent. of the observations the rotation was clockwise. Fig. 2 shows two stages of the formation of the glow.

Fig. 2.



Experiments showed that as the pressure in the tube is reduced, the bright bead passes farther through the hole and ends in a brush-like expansion. The bead occupies only the central part of the hole, and does not touch the circumference unless the plate is disconnected from the earth, in which case it becomes shorter and fills the entire opening. At lower pressures the bead becomes thinner and disappears suddenly. In hydrogen the bead does not end in a diffuse brush as with other gases which were used. Instead, it is very sharply defined. When copper electrodes are used the bead has the same length as with aluminium, but is much smaller in diameter.

It was found that the pressures at which the bead appears and disappears vary greatly with different gases and different metals used as cathode. Table I. shows the range of pressures over which the bead can be maintained with aluminium cathode and opening 2·6 mm. in diameter.

With copper electrodes the minimum pressure at which the bead could be maintained with helium was 1·34 mm., When dry air and a cathode of gold were used the minimum pressure was ·420 mm. On account of rapid sputtering, work with these cathodes was very difficult.

Table I.

	Minimum pressure.	Maximum pressure.
Oxygen–coal-gas	·120 mm.	·600 mm.
Oxygen	·130 ,,	·525 ,,
Air	·150 ,,	·700 ,,
Hydrogen–coal-gas	·197 ,,	·712 ,,
Hydrogen	·225 ,,	·912 ,,
Coal-gas	·380 ,,	·825 ,,
Helium	·625 ,,	1·12 ,,

No doubt the explanation, given by Sir J. J. Thomson *, of the passage of charged particles through an opening applies to the bead described above.

It was observed that when the cathode was concave towards the anode, the concentration of force before the opening prevents the passage of the bead. Plane or convex cathodes offer no such difficulties.

It was found that if, when the bead and glow have disappeared by pressure having been too far reduced, more gas is slowly let in, the reappearance of the bead and glow always occurs at a pressure which is higher than that at which disappearance occurred. If pressure is not too far reduced below this minimum, placing the hand or a layer of foil connected to earth on the tube between P and P′ will cause a reappearance. The reappearance is not brought about by placing an earthed conductor on the tube between anode and cathode. Placing a gauze over the glass wall between P and P′ and in contact with the cathode does not change the pressure at which appearance or disappearance of the bead and glow occur.

In the experiments with copper and gold cathodes, it was found that when the glass walls become well coated with metal sputtered from the cathode, the glow appears without the bead and continues even when pressures are very low. In this case the dark space is longer than the Crookes's dark space.

Experiments were made to determine the nature of the discharge between P and P′ by means of a strong electromagnet. Deflexions were such as to show that negative charges pass off from the metal surface on either side of P, and from P′ into the glow. A slight deflexion of the diffuse bead showed the presence of negative charges in that region.

* Phil. Mag. Dec. 1909, p. 842.

An examination of the bead and glow was made by means of a direct-vision spectroscope. The spectrum showed the lines characteristic of the gas in great brilliance, and superimposed upon this the bright lines of mercury vapour. The spectrum from either side of the plate P was the same. The spectrum of the glow between the plates showed the same lines, but of less intensity.

It was found that with each of the gases and gas mixtures experimented upon, the dark space covering the metal surface between the plates P and P′ increases in length as pressure is diminished, until the pressure is reached at which the bead and glow disappear. The Crookes's dark space is usually slightly longer than the dark space which appears behind the cathode. With hydrogen the dark space next to P′ reaches a maximum of 6·5 mm. when the Crookes's dark space reaches 7·5 mm. As soon as the glow is extinguished, the Crookes's dark space suddenly elongates to 11 mm. In coal-gas the dark spaces have lengths 6 and 7 mm. respectively, while air gives 4·5 and 7 mm. respectively. Helium with copper cathode gives 7·5 and 8·5 mm. respectively, and air with gold cathode gives equal dark spaces of 7·5 mm. length. In all cases the total current diminishes at the instant the bead and glow disappear.

When the opening in the plate P was made very large, 4 mm. diameter or more, it appeared that the glow never completely disappears with decreased pressure. However, at low pressures it becomes unsteady. At these low pressures a fine pencil of bluish rays passes through the opening. A magnet deflects this pencil in a direction which indicates that it is a stream of electrons passing towards the anode.

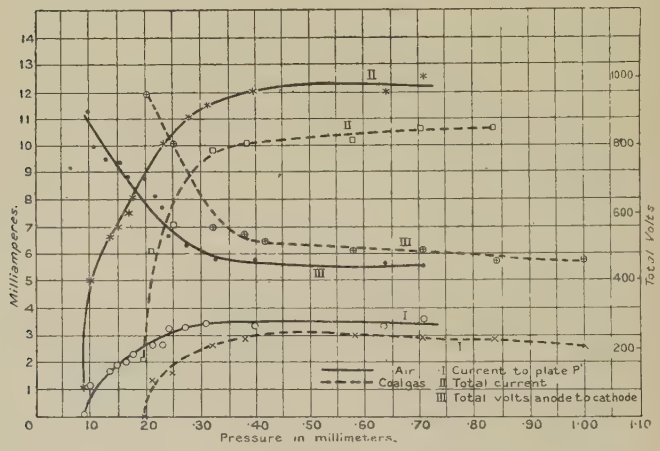
It was observed that when with copper or gold cathode the inside glass walls become well covered with sputtered metal, the glow could not be extinguished by reducing the pressure. Under these conditions all traces of a discharge through the opening were absent. The dark space at P′ reached to twice the length of the Crookes's dark space. The metal-covered glass walls between anode and cathode also caused the negative glow to recede from the glass, thus forming a distinct dark space there.

To determine the part taken in the discharge by each of the cathode plates, these were disconnected from each other and earthed separately. The current from P′ was measured by a galvanometer, while the total current was read from a milliammeter. Readings were started when the pressure had been sufficiently reduced to cause the glow to spread entirely to plate P′.

Fig. 3 shows the results of measurements taken in air and in coal-gas.

These graphs show that plate P′ carries approximately 30 per cent. of the current. It is seen that P′ carries a greater percentage of the total current in air than in coal-gas. It is also shown that even with higher total voltage, coal-gas yields smaller total current and also smaller current through P′ than does air.

Fig. 3.



With each of these mixed gases the current flowing through P′ increases slightly as pressure is decreased, until a maximum near the pressure ·65 mm. is reached. With lower pressures this current falls. The discharge between P and P′ continues to much lower pressures in air than in coal-gas.

The graphs of fig. 4 show the relation of partial current, total current, and total voltage for hydrogen and oxygen at various pressures. These gases were carefully dried by charcoal cooled with liquid air.

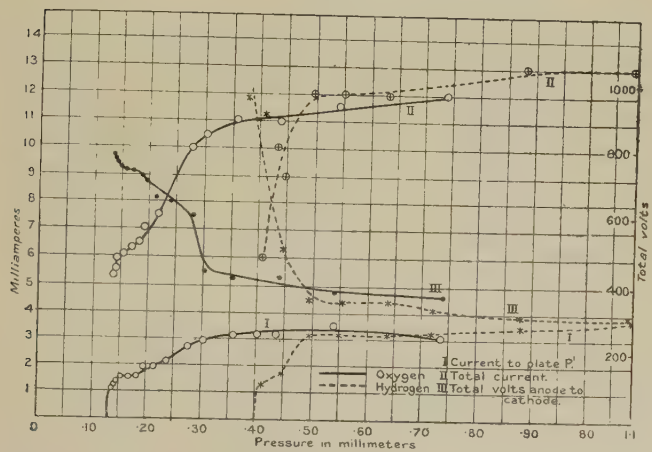
It is seen that the bead and glow can be continued to much lower pressures in oxygen than in hydrogen. The minimum pressure for air is lower than that for either hydrogen or oxygen.

The total anode cathode current is seen to be less in oxygen than in hydrogen although the total voltage is higher. The plate P′ carries a greater percentage of current in oxygen than in hydrogen.

Lower voltages were also found in the glow for hydrogen, and the pressure range at which the bead and glow are present was found to be shifted toward lower pressures compared with these other gases.

The flattening of the "knee" of each of the current curves of these four gases indicates a sudden reduction in the current. This is always accompanied by a flare at the end of the bright bead. But as pressure is reduced, there is a lingering of the discharge through the opening, until the pressure is reached at which sudden extinction occurs.

Fig. 4.



Experiments were made to determine the dependence of the presence of the bead and glow upon the size of the hole in the cathode. With air in the tube the following data was taken :—

Diameter of the opening.	Pressure at which bead and glow appear.	Pressure at which bead and glow disappear.
2·6 mm.	·42 mm.	·140 mm.
3·6 „	·80 „	·055 „

In the case of the larger opening the bead and glow became very unsteady at a pressure of ·175 mm. For these experiments, voltage was taken from an induction coil.

For measuring the potentials at points between the equipotential plates of the cathode, the probe O was connected to the electrometer as shown in fig. 1. The cathode system could be moved over a distance of 47 mm. On account of

the glass which shielded the probe, the latter could not be brought into contact with the plates P and P′.

Objection may be raised to the probe method of measuring potentials in the discharge. Langmuir * has shown theoretically that space-charge in a discharge region produces error in this method of measurement, and McCurdy † has shown experimentally that this error amounts to a few volts. It is believed, however, that the exact voltage of the points in the glow region described above does not vary appreciably from that shown in the graphs.

In order to test the method of measurement, the probe was placed between anode and cathode so that potentials of points in the Crookes's dark space could be measured. It was found that when the probe was placed at the limit of the negative glow, the whole potential fall was recorded to within 3 per cent.

Aston ‡ showed that the potential across the Crookes's dark space is very nearly equal to the total anode-cathode potential.

The following graphs (figs. 5 to 8 inclusive) show the results of the measurements of potentials in mixed gases.

Fig. 5.

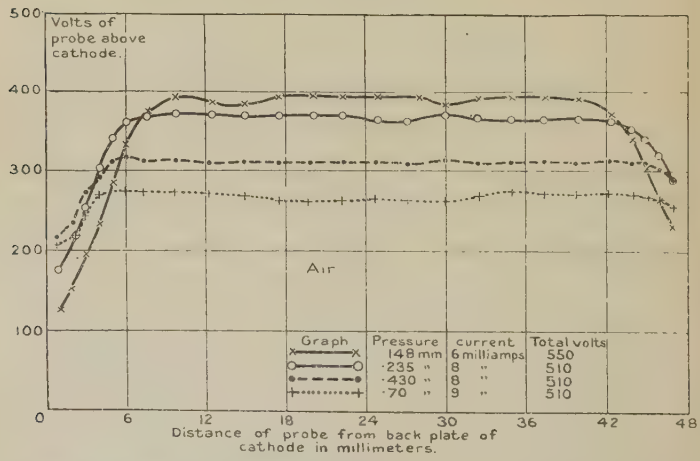


Fig. 5 shows the potentials in the glow produced in air. The pressures ·148 mm. and ·7 mm. represent the lowest and highest pressures respectively at which the bead and

* Langmuir, Journal Franklin Institute, Dec. 1923; General Electric Review, xxvi. p. 731 (1923).

† McCurdy, Phil. Mag. Nov. 1924.

‡ Aston, Proc. Roy. Soc. lxxxiv. p. 532 (1911).

glow could be maintained. The graphs of highest and lowest voltages in figs. 6 to 11 inclusive also represent the extremes of pressure at which bead and glow can be maintained. For all the potential measurements the hole in the cathode was 2·6 mm. in diameter. The cathode was aluminium.

In a table by Gunther-Schulze * the cathode fall of potential for air with aluminium cathode is given as 242 volts. Here, however, the fall of potential across the Crookes's dark space was about 500 volts, and the potentials of the glow were always about two-thirds to three-fourths of that amount.

Fig. 6.

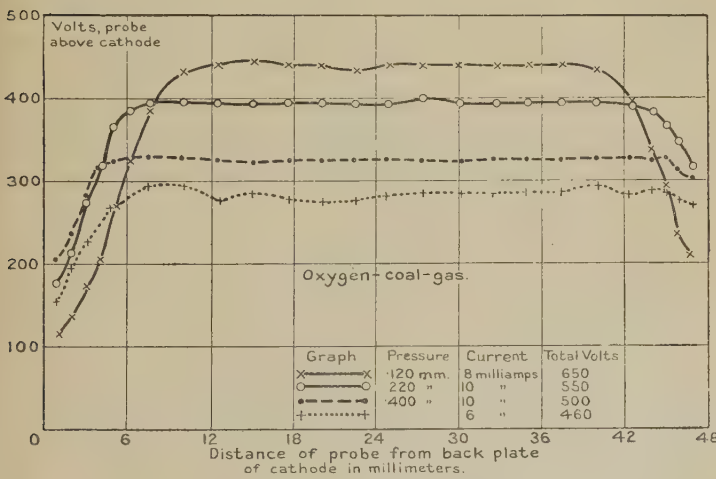


Fig. 6 shows the graphs representing potentials in a mixture of approximately equal volumes of oxygen and coal-gas. Here the pressures at which the glow begins and that at which it ceases are shifted towards lower pressures more than in any of the gases experimented upon. At the lowest pressure obtainable the dark space at P′ reached a length of 7·5 mm.

Fig. 7 shows the graphs representing potentials in the glow of a mixture of approximately equal p rts of hydrogen and coal-gas. While the pressure at which the glow appears is almost the same as that for air, the pressure at which it disappears is considerably higher.

* A. Gunther-Schulze, *Zeit. f. Phys.* no. 20, p. 6 (1923).

Fig. 8 shows the potentials in the glow of dry coal-gas. Here the uniformity of anode-cathode potential and total current is noticeable. There is more uniformity of dark space than with other gases. The pressure at which the

Fig. 7.

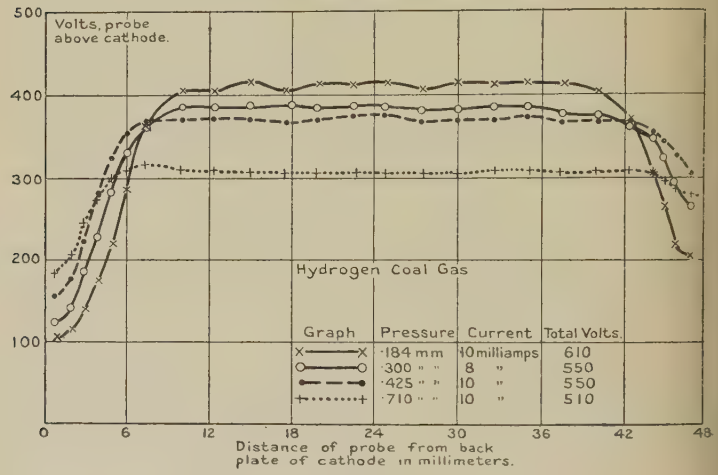
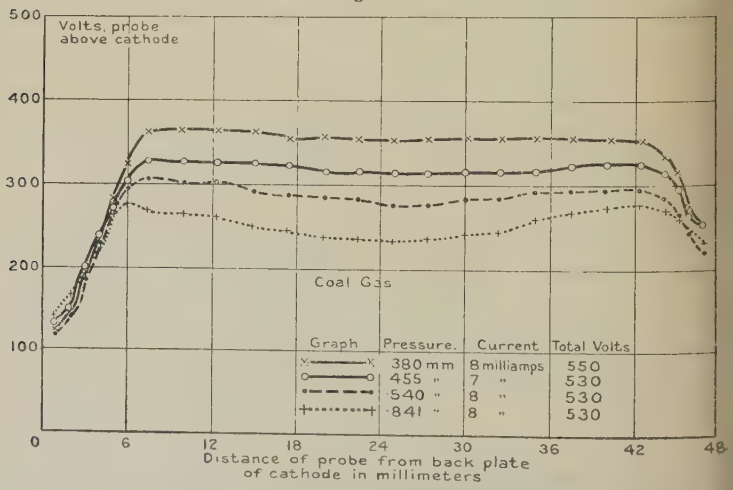


Fig. 8.



glow disappears is comparatively high. There is a tendency for the potential to fall in the middle of the glow region at higher pressures. The visible glow at these pressures was seen to be concentrated near the metal plates.

The following graphs (figs. 9, 10, and 11) show the potentials in simple gases. These gases were carefully dried by charcoal and liquid air before admitting them to the discharge-tube. This was also a means of taking air from the helium.

Fig. 9.

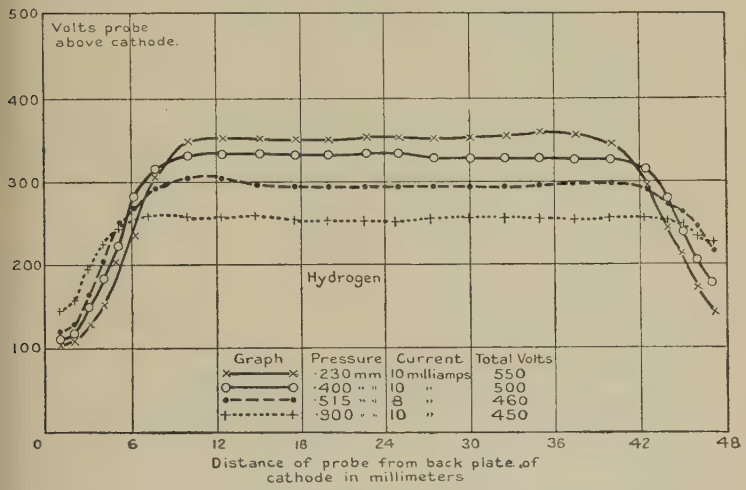


Fig. 10.

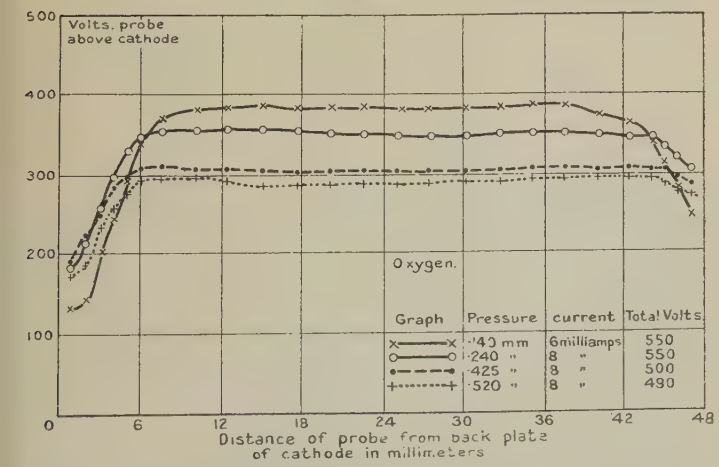


Fig. 9 shows the potentials in the glow of hydrogen. The gas was taken from a zinc-acid generator and very carefully dried. The potentials are appreciably lower than

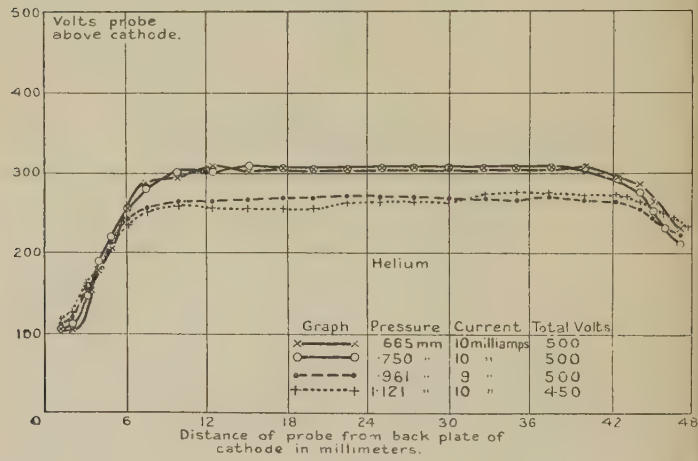
those at corresponding pressures in a hydrogen–coal-gas mixture.

The table* referred to gives the cathode fall of potential for hydrogen as 190 volts The graphs show that when 550 volts are applied to the tube, the potential between glow and cathode is nearly 360 volts.

Fig. 10 is the graphs of potentials in the glow in oxygen. The potentials are slightly lower than in air at the same pressures. They are considerably lower than those of oxygen–coal-gas.

Fig. 11 represents the potentials in helium. In this gas it was necessary to use higher pressures to obtain the bead

Fig. 11.



and glow than in any other gas. If pressures are taken into account, helium yields the highest potentials of any of the simple gases used. The table* gives 150 volts as the cathode fall of potential. This is lower than hydrogen or air. Disregarding pressure, the actual glow voltages here obtained are also lower than either hydrogen or air. The voltages of air, hydrogen, and helium obtained here bear very approximately the same relation to each other as do the cathode-fall potentials in these gases.

It will be observed that in each set of the above graphs, the potentials of the probe, going from the plates into the glow region, rise in a way which resembles the rise through

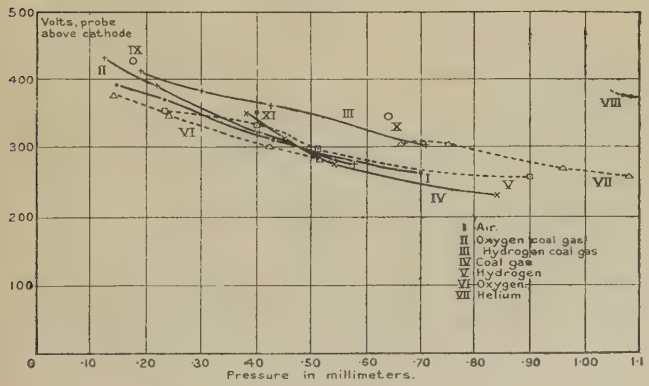
* A. Gunther-Schulze, *Zeit. f. Phys.* no. 20, p. 6 (1923).

the Crookes's dark space. Here, however, the maximum potential difference between cathode and glow does not exceed three-fourths of the total anode-cathode voltage.

The graphs show that in all gases experimented upon, the dark space next to the plates in the glow region increases in length as pressure decreases. There is not a corresponding fall in either the total current or the partial current passing through P′. The length of the dark space and the change in this length are not the same for all these gases. The potentials of the glow are always higher than that of the plates. As pressure is reduced this difference of potential increases. However, there does not seem to be a simple relation between potential and pressure.

The graphs of fig. 12, plotted from the data of the

Fig. 12.



preceding graphs, permit comparison of the gases in several respects. The curves of unbroken lines represent the gas mixtures, the others represent the simple gases. The short line VIII. indicates the voltages at which the bead and glow occur with helium and copper electrode. (The points should be shifted to pressures 1·34 and 1·44 mm.) The points IX. and X. represent the voltages in the glow of hydrogen and oxygen respectively with copper cathode, and point XI. represents that of air with gold cathode. Points VIII., IX., and X. indicate that complete data would yield a set of curves like those for the gases with aluminium cathode, except that the voltages would be higher at corresponding pressures. Points IX. and X. represent voltages in the glow, but with no bright bead passing through the opening.

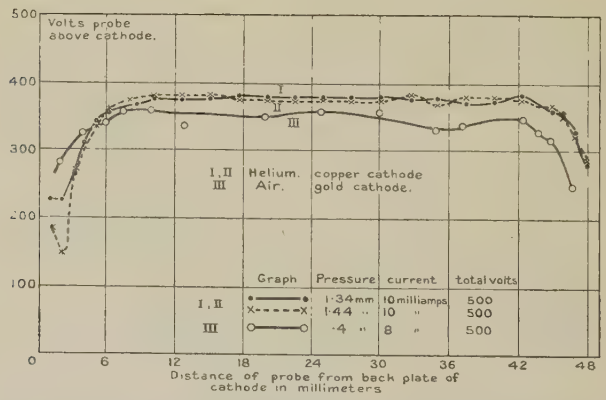
When the glass walls were sputtered with metal the bead failed to pass.

Fig. 12 shows that the gas mixtures as well as the simple gases vary widely in the range of pressures at which the bead will pass through the opening. This critical-pressure range depends upon the kind of gas and the material of the electrode. It is seen that oxygen gives lower potentials, and helium gives higher potentials, than the other gases at the same pressures.

Helium and hydrogen are exceptional in that near the low-pressure end of the range the rate of increase of voltage with decrease of pressure decreases in the case of hydrogen and increases in the case of helium.

The aluminium cathode was replaced by one of copper and potential measurements were made with helium. The dark space at P′ was slightly longer than when aluminium

Fig. 13.



was used, and the pressure range was shifted towards lower pressures. The bead was noticeably smaller in diameter. The potentials in the glow region were found to be very much higher than when aluminium was used at the same pressures.

Fig. 13 (I. and II.) shows that at each of the pressures there is a slight fall of potential near the plate P′. The cathode fall of potential* is given as 177 volts, which is seen to be much lower than the potentials of the glow.

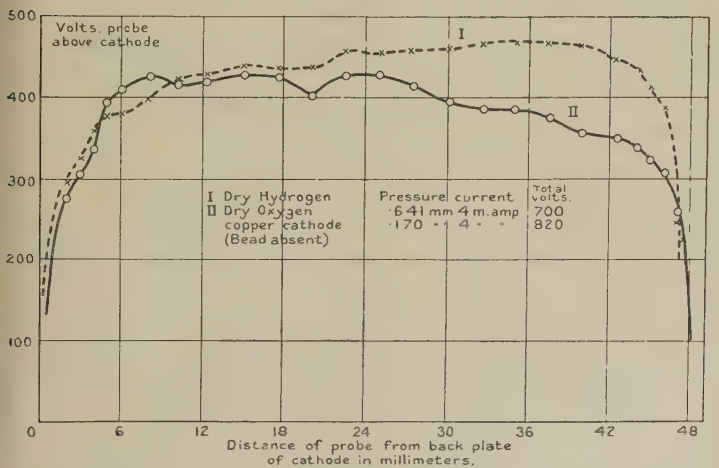
Graph III. (fig. 13) shows the potentials obtained in air, using a cathode. Here, again, the potentials are higher than the cathode fall, which is given as 297 volts.

* A. Gunther-Schulze, *Zeit. f. Phys.* no. 20, p. 6 (1923).

With copper and gold cathodes, rapid sputtering soon covered the inner walls with metal. Under these conditions it was found that the bead could not be made to pass through the hole. The glow, however, was readily produced.

Fig. 14 shows the graphs of potentials in hydrogen and oxygen with copper cathode and without the bead. The pressures at which the glow is produced vary widely. Comparing these potentials with those of figs. 9 and 10, it is seen that without the glow the potentials are much higher. It is seen also that the potentials for hydrogen are about 150 volts above the cathode fall.

Fig. 14.



With the probe set at a distance of 25 mm. from plate P′ the potentials of the glow with change of pressure were investigated. Oxygen and hydrogen were used and the bright bead was absent.

Fig. 15 shows the change in potential with pressure. It is seen that the potentials for these two gases vary widely at the same pressures.

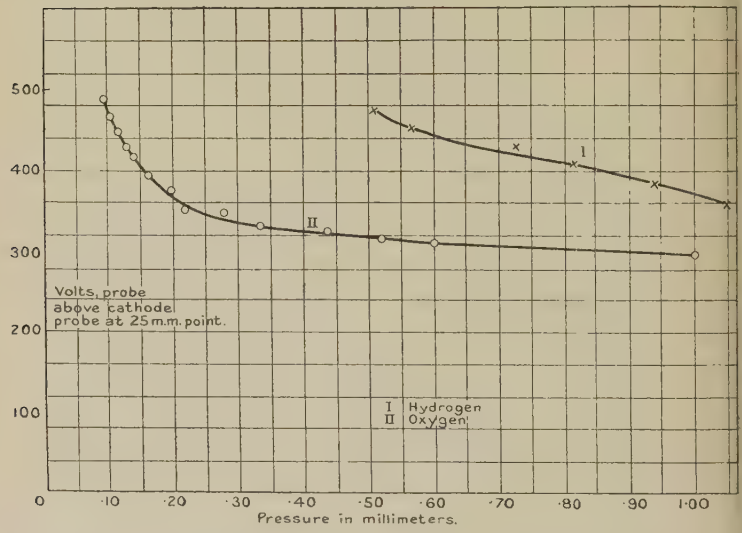
The pressures ·093 mm. for oxygen and ·51 mm. for hydrogen represent the minimum pressure at which the glow could be maintained. At these minimum pressures the dark space at P′ was approximately twice the length of the Crookes's dark space.

While working with the tube in the spluttered condition,

it was observed that in oxygen the glow between the plates P and P′ at a pressure of 1·18 mm. breaks up into striations. These were not observed with other gases.

In a recent paper, Schaufelberger * has shown that air, when carefully dried, gives 302 and 418 volts respectively with aluminium and gold for the normal cathode fall of potential. The potentials of the glow above that of the cathode for the same gases and cathodes, as found in the work here described, are 320 and 350 volts respectively. In

Fig. 15.



a table by Gunther-Schulze † the normal cathode fall for helium with aluminium and for helium with copper are given as 153 and 177 volts respectively. The potentials of the glow above the cathode as found here for the same materials are 360 and 370 volts respectively. The latter voltages are of the same order as those found by Schaufelberger for air. The table by Gunther-Schulze gives for the normal cathode fall in hydrogen with aluminium, in hydrogen with copper, and in hydrogen with gold, 192, 199, and 330 volts respectively. The values of the potential of the glow above the cathode, as found here, for the same gases and cathode are 300, 440, and 320 volts respectively.

* Schaufelberger, *Ann. d. Physik*, lxxiii. p. 38 (1924).
† A. Gunther-Schulze, *Zeit. f. phys.* no. 20, p. 6 (1923).

Summary.

Investigation has been made of the discharge of electricity between parallel and equipotential plates which form the cathode of a discharge-tube.

Important phenomena connected with the discharge are the presence of a bright bead passing through the hole in the plate nearest the anode, and a glow which fills the volume between the plates. The glow region has a dark space next to the metal surface. The length of the dark space depends upon the kind of gas, the gas-pressure, and the material of the cathode.

Investigation with a magnet showed that electrons are evolved from the metal surface between the cathode plates. At low pressures a cathode stream passes through the opening towards the anode.

The presence of electrons and the glow indicate an ionized state of the gas and the neutralization of the canal rays between the plates.

Spectroscopic examination of the bead and glow revealed the intense lines characteristic of the gas with the bright lines of mercury superimposed.

The maximum and minimum pressures at which the bead and glow can be maintained in different gases were determined.

Experiments were made to show the relation of total voltage, total current, and current flowing from the back plate of the cathode. Curves show these relations at different pressures.

Investigations to show the dependence of pressure-range and pressure of the bead and glow were made.

Potentials at points between the cathode plates were measured by means of a probe in air, oxygen–coal-gas, hydrogen–coal-gas, coal-gas, and the simple gases hydrogen, oxygen, and helium. Graphs show these potentials at different pressures.

Graphs are given which show the change in potential of the glow with change in pressure. It is shown that the range of pressure at which the bead and glow are present in different gases varies widely.

Experiments were made to determine the potentials in the glow with helium, using copper electrodes. These potentials are shown to be higher than those obtained with aluminium. Similar experiments were made with air, using gold as the cathode.

It was found that when the glass walls become coated

with sputtered metal the bead could not be produced. Measurements showed higher potentials in the glow under these conditions.

Graphs are given which show the change in potential in the glow with a reduction of pressure in oxygen and hydrogen when the bead is not present.

Conditions are discussed under which oxygen gives striations between the equipotential plates.

In conclusion, the writer wishes to express sincere thanks to Professor Sir J. J. Thomson, who suggested the problem and offered advice and criticism throughout the investigations. Thanks are also gratefully expressed for the fact that the resources of the Cavendish Laboratory were extended for carrying out the experiment.

The writer is grateful also to the President and Trustees of Indiana University for the grant of a leave of absence which made this research possible.

Cavendish Laboratory,
Cambridge,
June 1925.

CXXXI. *The Crystalline Structure of Hexachlorobenzene and Hexabromobenzene* *. *By* William G. Plummer, *M.Sc.*†

[Plate XXXV.]

I. *Crystallographic Information.*

THE following data are taken from Groth's *Chemische Krystallographie*, iv. p. 9 :—

Hexachlorobenzene $= C_6Cl_6$.

Monoclinic prismatic. Specific gravity 2·044 (Fels).
$a : b : c = 2{\cdot}0993 : 1 : 4{\cdot}322$. $\beta = 116° 52'$.

Habit : {001}, {100}, {10$\bar{2}$}, 11$\bar{1}$}; 30$\bar{7}$}, {702}.
Cleavages : {001} perfect ; {10$\bar{2}$} and {11$\bar{1}$} imperfect.

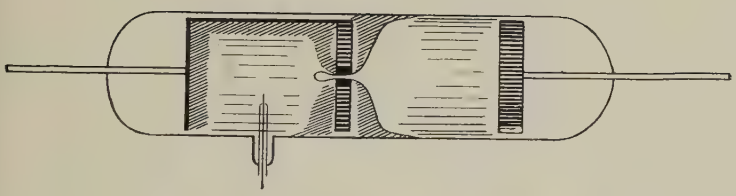
Hexabromobenzene $= C_6Br_6$.

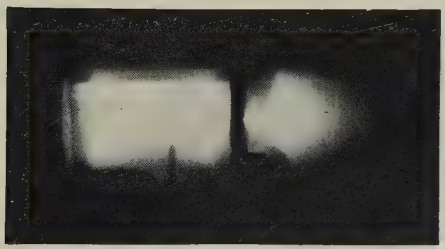
Monoclinic prismatic. [Specific gravity = 3·33, determined by Miss Yardley.]
$a : b : c = 2{\cdot}0903 : 1 : 4{\cdot}282$. $\beta = 116° 28\frac{1}{2}'$.

Habit : {100}, {001}, {11$\bar{1}$}, {1$\bar{1}$1}, {10$\bar{2}$}, {$\bar{1}$02}, {109}.
Cleavages : {001} perfect ; {10$\bar{2}$} and {11$\bar{1}$} imperfect.

* Incorporating the results of a Thesis approved for the Degree of M.Sc. in the University of London, submitted May 19, 1924, to which reference should be made for a more complete discussion. Similar results have since been arrived at by H. Mark, *Berichte der Deut. Chem. Gesellsch.* lvii. p. 1826, and published on November 5, 1924.

† Communicated by Sir W. H. Bragg, K.B.E., F.R.S.





II. *The Structure of Hexachlorobenzene.*

As the two crystals under investigation are isomorphous, a detailed consideration of the chloro-compound will suffice. The difficulty of growing sufficiently large crystals of either of these substances was responsible for the employment of the "powder" method of analysis, from which the present structure was determined. In June 1924, however, a small but perfect crystal of hexachlorobenzene was grown, showing the forms {001}, {100}, {10$\bar{2}$} and {11$\bar{1}$}. Subsequent spectrometer measurements and rotated crystal photographs of this crystal confirmed the suggested structure.

Table I. shows the spacings obtained from a series of

TABLE I.—Spacings for Hexachlorobenzene.

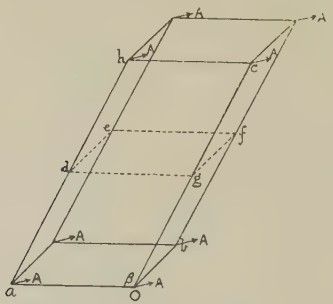
Observed intensity of reflexion.	Spacing observed. Å.	Corresponding theoretical spacing, assuming two molecules per cell. Å.	Theoretical plane.
Very weak to weak ...	7·4	$\frac{14·8}{2} = 7·4$	002
Very weak	7·2	7·22	100
Do.	7·0	7·00	10$\bar{2}$
Very weak to weak ...	4·29	4·30	102
Do. ...	4·16	4·16	10$\bar{4}$
Do. ...	4·07	$\frac{8·09}{2} = 4·04$	20$\bar{2}$
Moderate	3·85	3·86 or 3·87	010 or 20$\bar{3}$
Very weak to weak ...	3·73	3·73	011
Very weak	3·67	3·70	004
Moderate	3·59	$\frac{7·22}{2} = 3·61$	200
Strong	3·48	3·48, or $\frac{7·00}{2} = 3·50$	11$\bar{1}$ or 20$\bar{4}$ and possibly (012), (103)
Very weak to weak ...	3·17	3·17	111
Very weak	3·13	3·14	11$\bar{3}$
Do.	3·04	3·05 or 3·08	013 or 20$\bar{5}$
Weak to moderate ...	2·86	2·87	112
Moderate	2·83	2·83	104 or 11$\bar{4}$
Very weak	2·78	$\frac{5·58}{2} = 2·79$	202
Very weak to weak ...	2·75	2·76	21$\bar{1}$ or 10$\bar{6}$
Weak to moderate ...	2·69	$\frac{5·39}{2} = 2·69$, or $\frac{8·09}{3} = 2·70$ or 2·68	20$\bar{6}$ or 30$\bar{3}$ or 014

"powder" photographs taken with a Shearer X-ray tube fitted with a copper anticathode, the β-lines of copper having been excluded by the use of a nickel filter of suitable thickness. On the provisional assumption of two molecules per unit cell, the crystal data give the dimensions of the cell as $a=8{\cdot}10$ Å., $b=3{\cdot}86$ Å., $c=16{\cdot}68$ Å. ; from these values are calculated the figures in the third column of Table I.

A detailed examination of these results shows that the number of molecules per cell must be two ; also that the spacings of planes $(h0l)$ are halved if l is odd, (in consequence the planes $(20\bar{3})$, (103), $(20\bar{5})$ and $(30\bar{3})$ may be deleted from the fourth column in Table I.). These conclusions have now been corroborated by spectrometer observations by Miss Yardley, who found reflexions for the planes $(11\bar{1})$, $(1\bar{1}\bar{1})$, $(30\bar{2})$, (010), (100), (200), (002), (004), $(10\bar{2})$, $(20\bar{4})$, $(20\bar{2})$, $(20\bar{6})$, (102) ; whereas reflexions from the planes (003), $(10\bar{1})$, $(30\bar{3})$, (101), $(20\bar{3})$, $(20\bar{5})$ were absent. Possible doublings of the axial spacings and of the $(11\bar{1})$ were looked for, but not found.

Since the (010) plane is not halved, and planes $(h0l)$ are halved if l is odd, the space-group * for hexachloro- and hexabromobenzene is C_{2h}^4. The possible molecular symmetry is therefore a dyad axis or centre.

Fig. 1.



The determination of the position of the second molecule may now be attempted. Let the parallelopiped in fig. 1 represent the unit cell for hexachlorobenzene, and suppose one type of molecule, an A-molecule, placed at each of the vertices. The second or B-molecule is to be so placed that

* Astbury and Yardley, Phil. Trans. (A), ccxxiv. p. 221 (1924).

the (001) plane is halved by it, while the (010) and (100) planes retain their full spacing; it is obvious, therefore, that the B-molecule lies somewhere upon the line *de* or *gf*, these lines being parallel to the *b*-axis, and bisecting the (100) faces. A more exact specification of the position of this B-molecule is not possible if the molecular symmetry be a dyad axis, for in that case the plane of symmetry (010) will be due to structure, and a B-molecule is obtained by reflexion of an A-molecule in a plane parallel to the (010), followed by a translation of $c/2$. If, however, the molecule be supposed to possess a centre, then a B-molecule is obtained from an A-molecule by either a gliding-reflexion in the (010) plane or a rotation about the *b*-axis, *and in this case it must necessarily lie actually at the points d, e, etc.* That the B-molecule does really lie at or very near the points *d*, *e*, etc., is now confirmed by a rotation photograph of the single crystal about the *c*-axis, taken by Mr. Astbury (Pl. XXXV.). No spots (or extremely faint ones) appeared on the odd hyperbolæ (*hk*1), (*hk*3), (*hk*5), etc., and although the fact that planes (*h*0*l*) are halved if *l* is odd tends to weaken these hyperbolæ, something further would be required to completely obliterate them, namely, that the B-molecule lies upon the *c*-axis and halfway down it.

One cannot say with absolute certainty what is the molecular symmetry in hexachlorobenzene, but the fact that the reflexion molecule is found experimentally to lie halfway down the *c*-axis makes it extremely probable that the molecules are centro-symmetrical; for space-group theory demands that centro-symmetrical molecules in this group shall lie exactly in the positions arrived at for this substance.

Previous work upon naphthalene and benzene also favours the adoption of a centro-symmetrical molecule, for this type of molecular symmetry was found for naphthalene * and anthracene † by Sir William Bragg, and for benzene ‡ by H. Mark.

III. *Suggested Arrangement of the Atoms in the Molecule.*

The remainder of this paper is to a certain extent speculative. Assuming the measurements of the "puckered" benzene ring introduced by Sir William Bragg (presumed the same as in naphthalene—carbon "diameter" = 1·50 Å., and the carbon atoms linked at the tetrahedral angle), and

* W. H. Bragg, Proc. Phys. Soc. Lond. xxxiv. (1) p. 33 (1921).
† W. H. Bragg, Proc. Phys. Soc. Lond. xxxv. (3) p. 167 (1923).
‡ H. Mark, *Ber. der Deut. Chem. Gesellsch.* lvii. p. 1826 (1924).

taking the original value obtained by W. L. Bragg for the chlorine "diameter" (2·10 Å.), various trial arrangements of the chlorine atoms lead to the structure indicated in figs. 2 and 3, which are drawn to scale and represent only

Fig. 2.

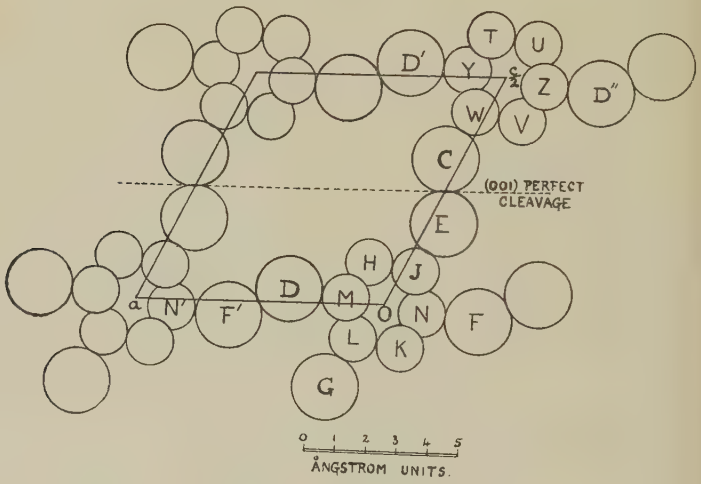
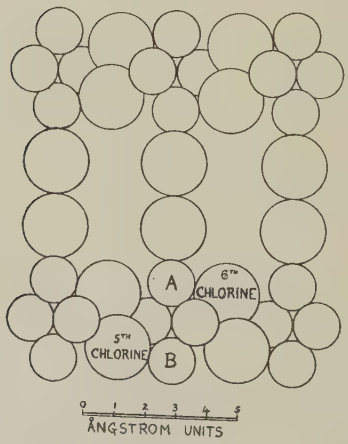


Fig. 3.



The two carbons immediately behind A and B in the benzene ring are hidden from view; in the molecule under consideration, the 5th chlorine is attached to the *front* carbon B, while the 6th is joined to the carbon *in rear of* A.

half the unit cell in the direction of the *c*-axis. In fig. 2, which shows the (010) face, the benzene ring TUZVWY has been tilted so that the carbon atoms T, U, V, W lie in the plane of the paper (or (010) plane of the cell), while the centre of the carbon atom Y is below, and that of Z is above, the plane of the paper at a distance of 0·71 Å. The chlorines C and E lie (*i. e.*, have their centres) in the plane of the paper; but chlorines D′ and D″ lie 0·71 Å. below and above that plane respectively. The next molecule, to which the benzene ring HJNKLM belongs, is obtained by a gliding reflexion in the (010) plane or a rotation about the *b*-axis of the molecule just considered; hence the carbons H, J, K, L and the chlorines E and G lie in the plane of the paper, while carbon M and chlorine D are "up," carbon N and chlorine F are "down"; chlorine D is "up," but chlorine F′ and carbon N′ are "down," and so on throughout the structure. Of the six chlorine atoms per molecule, the positions of four are explained in fig. 2; the remaining two occupy the positions indicated in fig. 3, which represents a view of the (100) face, and it can be readily shown by a scale model that with this arrangement of the chlorine atoms a good "fit" is obtained, and the experimental results and symmetry are complied with.

The perfect cleavage along the (001) plane is clearly to be expected from fig. 2, and an imperfect one approximately parallel to the $(10\bar{2})$ plane is not improbable. To illustrate satisfactorily the imperfect $(11\bar{1})$ cleavage plane the model is required.

IV. *The Structure of Hexabromobenzene.*

Assuming that the atomic "diameter" of bromine is 2·38 Å.*, and replacing the chlorine atoms in the chloro-structure by bromines, but keeping the orientations of the latter with respect to the benzene ring the same as those of the chlorines in the chloro-structure, careful drawing shows that an increase in the *a*- and *c*-axes of the hexachlorobenzene cell to $a=8{\cdot}50$ Å., $c=17{\cdot}6$ Å. is involved. These values are in agreement with the theoretically calculated values for the hexabromobenzene cell, $a=8{\cdot}57$ Å., $c=17{\cdot}6$ Å. Rough determinations of the *b*-axis by drawing give as a mean, $b=4{\cdot}2$ Å., which compares satisfactorily with the theoretical value, $b=4{\cdot}10$ Å.

It is inadvisable to place too much confidence in these

* W. L. Bragg, Phil. Mag. xl. p. 177 (Aug. 1920).

agreements on account of uncertainties regarding "atomic diameters"; if, however, the suggested structure of these compounds is correct, it affords a good example of isomorphous replacement after the manner indicated by the classic researches of Dr. E. A. L. Tutton.

Very little success attended the many efforts to obtain good powder photographs of hexabromobenzene, but the following spacings (Table II.) suffice to prove the general correctness of the structure.

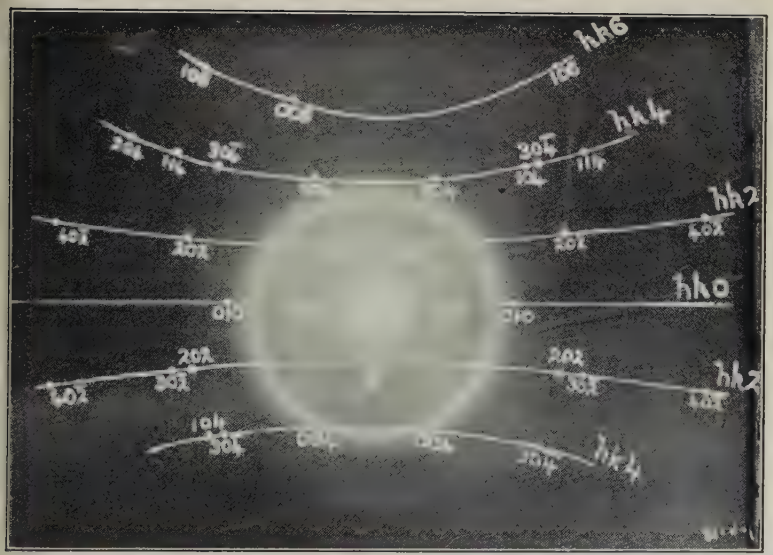
TABLE II.—Spacings observed for Hexabromobenzene by the Powder Method.

Observed intensity of reflexion.	Observed spacing. Å.	Theoretical spacing calculated from crystal data, two molecules per cell. Å.	Corresponding theoretical plane.
Very weak to weak ...	4·39	4·41	$10\bar{4}$
Weak to moderate ...	4·15	4·10	010
Strong; double line...	3·77	3·83 3·70	200 $11\bar{1}$ or $20\bar{4}$
Weak	3·36	3·37	111
Moderate	3·00	3·00	104 or $11\bar{4}$

It is of interest to note that the comparative shortness of the *b*-axis in these compounds places a very considerable limitation upon the chlorine and bromine atomic "diameters"—it would be almost impossible to fit a chlorine atom whose diameter is greater than 2·5 Å.

In conclusion, the author wishes to express his thanks to Professor Sir William Bragg, F.R.S., in whose laboratory this research was undertaken, for his kind interest and encouragement; to Mr. W. T. Astbury for his helpful criticism and advice; and to Miss Yardley, whose assistance in confirming the structure by spectrometer measurements was much appreciated. He is also indebted to the Department of Scientific and Industrial Research for the financing of this investigation.

Davy-Faraday Research Laboratory,
Royal Institution, W. 1.
July 27, 1925.



Rotated Crystal Photograph of Hexachlorobenzene about the *c*-axis.

For the sake of clearness, the distinct spots on the plate have been dotted in before printing. The light circle is due to the wax upon which the crystal was mounted.

CXXXII. *Determination of Size of Colloidal Particles by means of Alternating Electric Fields.* *By* Prof. E. F. Burton *and* Miss B. M. Reid, *M.A.**

THE particles of a colloidal solution remain indefinitely in suspension in the liquid medium, *e.g.* water, in spite of the fact that the density of the material of which the particles consist may be many times that of the medium. A calculation of the limiting velocity of settling under gravity and of the velocity due to the Brownian movement shows that for any given material there is a critical size of particle for which these two velocities are equal to one another †. For all particles smaller than this the Brownian movement masks entirely the gravitational settling, and consequently the suspensions are permanent; for example, there exist at the present time in the Royal Institution, London, samples of gold colloidal solutions in water prepared some seventy-five years ago by Faraday.

In a paper by one of the writers ‡, a method was suggested whereby the use of an electrical field in an auxiliary capacity might enable one to determine the limiting velocity due to gravitation in spite of the Brownian movement.

When a vertical electric field is applied to a colloid in a U-tube (fig. 1) there is a migration of the particles toward one electrode and away from the other depending on the charge of the colloidal particle. *If an electric field is applied which gives a motion to the particle greatly in excess of either the gravitational or Brownian movement*, the comparatively insignificant gravitational force will be added to the electrical for downward motion and subtracted for upward motion. If the field is applied in one direction for one period of time and then in the opposite direction for an equal period of time, one deals with a motion which is caused during the first period by the force $(Xe+mg)$ and during the second period by $(Xe-mg)$, where X=the electric field maintained in the liquid, e=the effective charge on the particle, and mg=gravitational pull on particle. The difference between the up and down motion will then he due to the settling caused by gravity, and to this motion Stokes' law can be applied.

* Communicated by the Authors.

† Burton, 'Physical Properties of Colloidal Solutions,' 2nd. Ed. p. 90.

‡ *Loc. cit.* p. 126; Proc. Roy. Soc. Lond. A, xcv. pp. 480–3 (1919).

If V = the limiting velocity due to the electric field,
v = the limiting velocity due to gravitation,
a = the radius of the particle, and
η = the coefficient of viscosity of water,

then from Stokes' formula

$$Xe + mg = 6\pi\eta a(V + v),$$
$$Xe - mg = 6\pi\eta a(V - v) ;$$

subtracting these,

$$2mg = 12\pi\eta av.$$

Since $mg = \frac{4}{3}\pi a^3(\rho - \rho')g$, where ρ, ρ' = the densities of the particle and medium respectively,

$$a^2 = \frac{9}{2}\frac{\eta v}{(\rho - \rho')g},$$

which gives a in terms of v.

This velocity may be obtained from observation of the settling in the U-tube over extended periods of time when an electric field has been applied for equal intervals in opposite directions. The settling observed is obviously due to gravitation alone and, if divided by the time of application of the field, gives v.

This method has been utilised in an attempt to determine the effect of the addition of different amounts of electrolytes on the size of the colloidal particles.

Experimental Method.

A number of copper sols were prepared by sparking with an electric arc underneath the surface of samples of conductivity-water containing increasingly larger traces of potassium hydroxide.

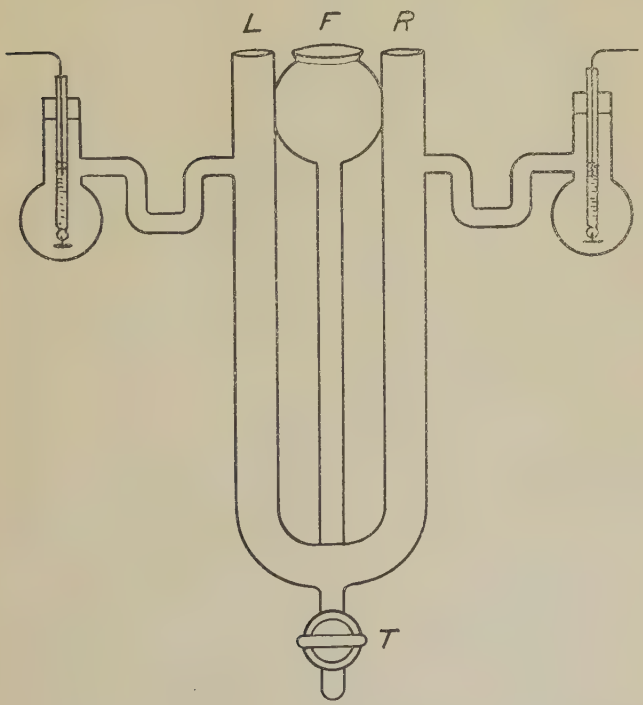
The U-tube used (fig. 1) was a slight modification of that ordinarily employed *.

The arms of the tube were each about 15 cm. long and 1·5 cm. in diameter; they were graduated in millimetres. Into the bottom of the U-tube was sealed a fine delivery tube provided with a tap T and a funnel F ; this tube was bent round so as to run up behind the arms and bring the funnel to the same height as the top of the U-tube. In addition, fine U-shaped tubes partly plugged with glass wool were sealed, one into each arm of the U-tube, 3·5 cm. from the

* *Loc. cit.* p. 138.

top; each tube communicated with the neck of a small glass bulb in which the electrodes were placed. In this way diffusion of the impurities which arise in the vicinity of the electrodes was prevented, and hence any settling or coagulation of the solution in the U-tube due to contact with these impurities was obviated.

Fig. 1.



The solution to be tried was poured into the funnel; the tap being closed, and water having a specific conductivity equal to that of the colloid was poured into the U-tube so as to partly fill it and also into the small side bulbs. The whole tube was placed in a water bath. The colloid was slowly introduced into the U-tube by a slight opening of the tap T. Care was necessary to keep the surface between the colloid and the water distinct. The tap was closed when the colloid had risen a suitable distance in the U-tube.

The conductivity of the liquid in the tube was measured

before and after each velocity determination, and it was found, in each case, that there was such a slight rise in conductivity that one would be justified in concluding that there was practically no diffusion of impurities from the neighbourhood of the electrodes.

The source of E.M.F. used was an 80-volt storage battery. The battery B was connected to a reversing-key K with mercury cups, and thence to the electrodes EE (fig. 2).

Fig. 2.

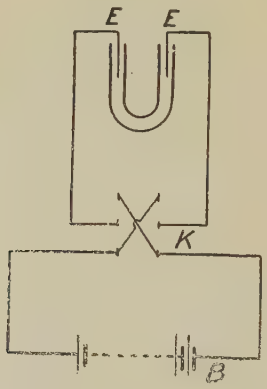
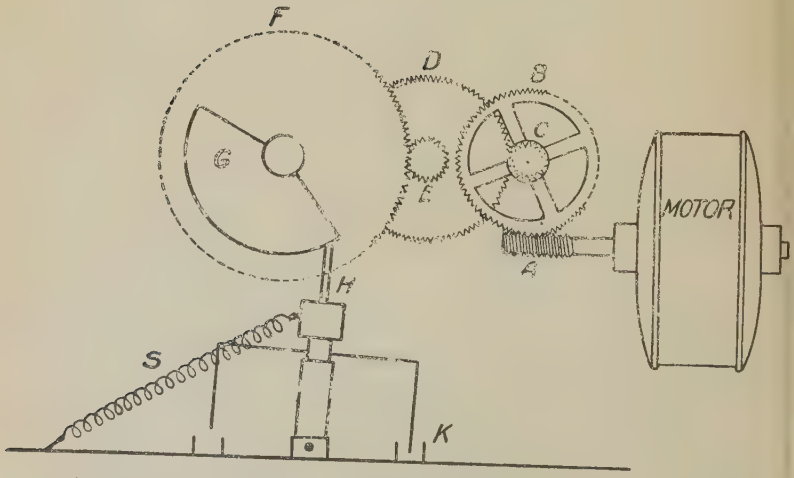


Fig. 3.



A mechanism was devised to turn the key about every minute and a half (fig. 3). A motor, the speed of which could be adjusted by means of a variable resistance in series

with it, turned a steel worm A, 1·5 cm. in diameter. The worm turned a cogged wheel B, 7·5 cm. in diameter and the motion was transferred by other cogged wheels C, D, and E, of diameter 1·2, 8·0, and 1·2 cm. respectively, to a large cogged wheel F, 12·5 cm. in diameter. A brass plate sector G, about ·5 cm. thick, was screwed on to the face of F, and a brass strip H, 2 cm. in length, 1·5 cm. wide, and 2 mm. thick, was attached in a vertical position to one end of the handle of the reversing-key K. One end of a spiral spring S was attached to the centre of the handle of the key and to the platform on which the apparatus stood. As the wheel F rotated, the sector G pushed against the strip H and forced the key over in opposition to the action of the spiral spring. When the cog-wheel F had completed a certain fraction of a revolution, the key was released by the brass plate G and pulled back again by the spring S. The speed of the motor was adjusted until the time of revolution of F was about three minutes, so that the current was reversed approximately every one-and-a-half minutes.

The settling in the U-tube was observed over a period of seven hours in each case; the results are given in Table I.

Table I.

Drops of $\frac{N}{100}$ KOH in 200 c.c. water used in sol.	Time field applied.	Settling in cm.	v in cm. per sec.	a in cm. calculated from $a^2=\frac{9}{2}\cdot\frac{\eta v}{(\rho-\rho')g}$.
0	7 hrs.	·225	$·89\times10^{-5}$	$7·14\times10^{-6}$
6	7 „	·252	$1·00\times10^{-5}$	$7·57\times10^{-6}$
18	7 „	·300	$1·19\times10^{-5}$	$8·26\times10^{-6}$
24	7 „	·325	$1·29\times10^{-5}$	$8·60\times10^{-6}$

The table shows an increasing size of particle for increasing amounts of potassium hydroxide added to the water. The colloid prepared in the sample of conductivity water, to which 30 drops of $\frac{N}{100}$ KOH had been added, coagulated in a short time, showing that the size of the particles had increased to such an extent that the Brownian movement no longer masked the effect of gravity.

One can compare the velocity due to gravitation with that due to the Brownian movement by use of the formulæ:

For gravitation $v_g = \frac{2}{9} \cdot \frac{(\rho - \rho')g}{\eta} \cdot a^2$,

For Brownian movement $v_B = \sqrt{\frac{RT}{N} \cdot \frac{1}{3\pi\eta} \cdot \frac{1}{t} \cdot \frac{1}{a}}$,

where R, T, and N have the ordinary significance.

A few such results are given in Table II. for copper particles ($\rho = 8{\cdot}9$) in water at 15° C.

TABLE II.

"a" Radius of Particle.	$v_g = 1{\cdot}7 \times 10^5 a^2$.	$v_B = 6 \times 10^{-7} \cdot \frac{1}{\sqrt{a}}$ ($t = 1$ sec.).
5×10^{-5}	43×10^{-5}	9×10^{-5}
1×10^{-5}	$1{\cdot}7 \times 10^{-5}$	20×10^{-5}
5×10^{-6}	$\cdot 43 \times 10^{-5}$	30×10^{-5}
1×10^{-6}	$\cdot 017 \times 10^{-5}$	60×10^{-5}

From this table we see that even with the theoretical formula for the Brownian movement, which cannot claim precise exactness, the size of particle for which the velocities due to gravitation and the Brownian movement become equal to one another is not very far removed from that indicated in Table I.

Summary.

A method of using a vertical alternating electrical field to move colloidal particles up and down in a tube and thus induce a true gravitational settling has been tested for the determination of the size of colloidal particles of copper in water.

CXXXIII. *On the Metric of the Four-dimensional Space-time Continuum.* *By* D. Meksyn *.

§1. *Introduction.*

THE present paper has as its aim to show :—

i. *In the special theory of relativity :*

That, starting from the conception of a four-dimensional space-time continuum, we can derive not only the constancy of light-propagation and the Lorentz transformations, but also the whole mechanics of a material point as geometrical laws in four-dimensional space ; so that the idea of relativity of time and space becomes not only superfluous, but is in sharp contradition to the assumption that our continuum is a metrical one in Riemann's sense. The present paper also demonstrates that the sizes of bodies, intervals of time, and mass are not affected by motion as such.

ii. *In the general theory of relativity :*

Developing some ideas of Einstein and Riemann about the metric of a space, we show that the measured distance between two points, which in Euclidean space has always the same numerical value (if the unit of measurement is fixed) and does not depend on the particular kind of measurement, loses its sense in the non-Euclidean space. In the latter the results of measurement depend on the material of our physical instruments, their form, construction, place of measurement, and so on ; all these results are different, and there is no reason why one should be preferred to another, nor any possibility of making them agree in the frame of non-Euclidean space ; so that the conception of a metric of a space as such has no sense if applied to non-Euclidean space. Hence such a space cannot be used as a general system of reference for physical laws.

I. Euclidean Space of Three Dimensions.

§ 2. *Geometrical figures and physical bodies in Euclidean space.*

Euclidean geometry assumes that a geometrical figure does not become changed if transferred from one part of space to another. The space immediately surrounding us

* Communicated by Mr. F. S. Spiers, F.Inst.P.

can be considered as Euclidean within the limits of our measurement, and at the foundation of our experimental physics lies the idea that not only a geometrical body but a real solid body does not become changed if transferred from one part of space to another; that is, no physical phenomenon has been discovered which indicates such a change. We always make corrections in our physical measurements to allow for changes of temperature, pressure, stress, and so on, but we never introduce a correction to allow for the mere change of position of a solid body in space.

§ 3. *Measurement of length in a "stationary" space.*

Now let us consider the process of measurement of lengths in Euclidean space, assuming that the observer and the measured body are at rest relative to our space (later on we omit this restriction). We could also measure the components of motion of a body, but if the measurement is carried out by light-signals, the latter must be sent out from our space and not from the moving body. In this sense we call such space "stationary." In such a "stationary" space the measured distance between two points, that is the number which we obtain as a result of our measurement, does not depend upon the particular kind of physical principle which we use for the measurement, if only we fix units and introduce the necessary corrections which exclude the influence of the particular physical principle itself.

In geometry we start from the notion of an absolutely rigid body; all measurements are carried out by a direct superposition, but in physics we use elastic bodies and different means—direct superposition, light-signals, and complex physical phenomena. The materials of our instruments are different, and yet we suppose that the result must be the same, and use different means only for convenience' sake. In principle they are all identical; that is to say, there is no experiment which shows a discrepancy due to the kind of measurement itself which has not been allowed for.

For this reason we will consider the distance between two points in such a space as "absolute," and may call such a metric "universal."

§ 4. *Measurement of time in a "stationary" space.*

In a "stationary" space we can define a scale of time. If we imagine similar clocks in several parts of our space, then using some physical phenomenon, which propagates uniformly and with the same velocity in all directions, we

can make all the clocks synchronous. So if we send a light-signal from A (at t_A), and it comes to B (at t_B) and, reflected, returns back to A (at t'_A), we say that the clocks in A and in B are synchronous if

$$t_B - t_A = t'_A - t_B \text{ *}.$$

In this way all clocks can be made synchronous, and the duration of every event is the same for all observers ; two events which are simultaneous for one observer are also simultaneous for all observers in this space.

In our measurement of time we assume that the material of the clocks is not changed during a long interval of time or if transferred from one place to another, and that the material and the construction of the clocks, and generally the particulars of measurement, have no influence upon the result.

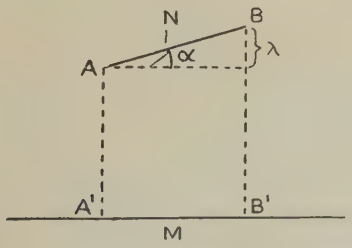
We assume this within the limits of our observations, and in that sense we can say that a stationary Euclidean space has an "absolute" time.

§ 5. *Measurements in a "stationary" space by light-signals.*

Now let us consider some instances of measurement of lengths and intervals by means of light-signals in a "stationary" Euclidean space. If the observer is in the immediate vicinity of the phenomenon, he gets the intervals by direct reading of clocks, and the distances by direct superposition of gauges. Both these measurements are independent of one another ; the first serves to measure only time, the second only space.

This phenomenon appears quite different if the observer and the measured object are widely separated, and the measurements are carried out by means of light-signals.

Fig. 1.



For example : Let the observer in M measure the length AB in N in this way (AB is in the same plane as A′B′, so

* See A. Einstein "Zur Elektrodynamik bewegter Körper," § 1, *Ann. d. Phys.* p. 17, 1905.

that it appears to the latter as parallel). Four observers are at the points A, B, A′, B′; they send from A and B light-signals towards M, and the observers at A′ and B′ are reading the gauges. It is clear that, generally speaking, the received length will not be l, but say $l\cos\alpha$. It is possible to find the length of AB in this way :—A and B send their signals simultaneously ; it is clear that B′ will receive it a little later than A′, say after τ sec., then our length is

$$=\sqrt{|A_1B_1|^2+\tau^2c^2},$$

where c is the velocity of light-propagation and AA′ and BB′ are perpendicular to A′B′.

Hence we see : to measure lengths by light-signals we must measure also time ; and in this particular case, when $A'B'=0$ we obtain the whole length by a time-measurement.

Let, now, an observer in M measure the time of passage of a body from A to B, again by light-signals (the signals are sent out from the space and not from the moving body).

At the beginning of the motion, A sends a signal to A′, and at the end B sends a signal to B′, and all are reading their clocks. It is clear that if the duration of this phenomenon is t for N, it will appear as $t'>t$ for M, where

$$t'=t+\frac{\lambda}{c};$$

and again to have the correct value t, the observer at M must not only measure time but also the distance λ, and introduce a correction due to the finite velocity of light.

II. Euclidean Space-time Continuum of Four Dimensions, or the Special Theory of Relativity.

§ 6. *Measurement of lengths and intervals in moving systems, and the relativity of time and space.*

Now we start with the special theory of relativity; and first let us consider the train of ideas which brought Einstein to his conception of relativity of time and space. His reasoning began from the description of measurement of lengths and intervals by light-signals. The general arrangement of his experiment is the same as in our § 5. Only AB is parallel to A′B′, and is moving with a constant velocity v relative and parallel to A′B′.

If A and B simultaneously (according to their clocks) send light-signals from the moving system N, and A′ and B′

read their gauges simultaneously (according to their clocks) in M, the measured length of AB in M and in N will not be the same.

Again, if A′ and B′ check their clocks by light-signals according to § 4, and find them synchronous, the observers in A and B, who are in motion relative to M, will not find them synchronous.

Hence the Theory of Relativity concludes that the conception of simultaneity has no absolute significance; an event which two observers find simultaneous another two in relative motion will not consider so.

Now the question arises: Why do we receive different results if we measure a moving rod and a stationary one by light-signals? Is it due to the relativity of lengths and intervals, or because we have not introduced the necessary corrections into our measurements?

The Theory of Relativity supposes that, carrying out our measurements from moving systems by means of light-signals, we get our results by direct reading of the clocks and gauges; but we have seen that even in a "stationary" space, where an "absolute" time and space can be defined, we never get the final results of measurements by a direct observation; if the measurements are carried out by light-signals, we must always introduce a correction due to the finite velocity of light.

And even more so; in every physical measurement we never get our final results by a direct observation, but must always introduce a correction in our measurement which excludes the influence upon our final results of the particular kind of phenomenon which serves us for this measurement.

In our case all corrections are due to the law of propagation of light in moving systems. The question is only in what manner these corrections must be applied.

§ 7. *An observer in one dimension.*

A simple instance will make the matter clear. Let us have in a "stationary" Euclidean space, where time and space are "absolute," an observer who conceives the physical world of phenomena only in one dimension. How will the world of phenomena appear to him? Along his line of observation, lengths and intervals will be "absolute," but they will lose this character for every phenomenon in higher dimensions if it is observed by light-signals. So the length AB, which for the observer at M is equal to $AB = l$, for our observer at N is only equal to $A'B' = l \cos \alpha$.

Let him observe a uniform motion of a body from A to B. The travelled distance will be $l\cos\alpha$, the duration of motion $t+\frac{\sin\alpha}{c}$ (where t is the duration which the observer at M will measure), and the velocity of motion

$$v=\frac{l\cos\alpha}{t+\frac{l\sin\alpha}{c}}<\frac{l}{t}=v;$$

that is, all processes will appear slower to him ; and when AB is perpendicular to A′B′, time will "stop" because the body will have to travel an infinite interval of time before its motion will be observed along the line of A′B′. So that our observer, if he is not conscious of the second dimension, will be led to the conclusion that time and space are "relative."

But for the observer in two or three dimensions there will exist no "relativity," and he will explain the "contraction" of lengths and the non-synchronism of clocks by the rule of projection in connexion with the finite velocity of light.

Our case presents a similar phenomenon ; therefore let us now investigate the necessary corrections arising from the law of constancy of light-propagation, and starting from the conception of a four-dimensional continuum (where the fourth dimension will be time).

From this conception it follows that two three-dimensional spaces which are in relative uniform rectilinear motion are equivalent in our scheme to two four-dimensional continua whose axes of time are relatively inclined ; therefore the necessary corrections must follow from a transformation of coordinates of two such spaces. As it is known, the Lorentz transformations are a particular case of such transformation.

We shall not give the derivation of the Lorentz transformations as a kind of rotation of axes of coordinates here, as it can be found in many papers on the theory of relativity.

If x', l' and x, l are respectively the coordinates of time and space in a system moving with velocity v and in a stationary system, the Lorentz transformations are

$$x'=\frac{x-vl}{\sqrt{1-v^2}},\qquad l'=\frac{l-vx}{\sqrt{1-v^2}}.$$

Hence we see that if by direct measurement of a length or an interval of a moving system we obtain the results

Δx and Δl, the true values will be $\Delta x' = \frac{\Delta x}{\sqrt{1-v^2}}$ and $\Delta l' = \Delta l \sqrt{1-v^2}$, or the lengths must be increased and the intervals diminished.

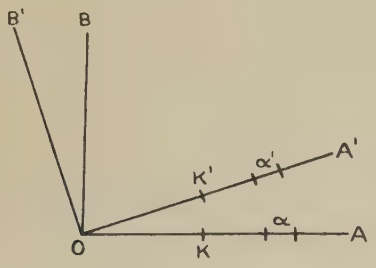
§ 8. *The relativity of time and space and the metric.*

Let us now consider the ideas of relativity more in detail. For simplicity we use only two dimensions (x, l). Let us have a system at rest AOB, a rod at rest OK, and a standard α; the length of our rod is $\frac{\overline{OK}}{\alpha}$. The rod receives a uniform rectilinear motion so that its length and its space at rest will be OK′ and A′OB′ respectively and its stardard α'.

According to our ideas, $\overline{OK'} = \overline{OK}$ and $\alpha' = \alpha$; according to the Theory of Relativity, OK′ is objectively less than OK, $\alpha' < \alpha$, and $\frac{\overline{OK'}}{\alpha'} = \frac{\overline{OK}}{\alpha}$ (law of relativity), so that all lengths are contracted $\sqrt{1-v^2}$ times.

We think that the latter view is incorrect, because, in order that a metric shall exist, it is necessary that the length of

Fig. 2.



every line shall be independent of its position, or that every line shall be measurable by every other. It is Riemann's main condition *. Either we accept the relativity of time and space, and our space-time continuum is therefore not a metrical one in Riemann's sense, or we must reject the conception of relativity. A uniform rectilinear motion might conceivably produce a curvature of space and time (this conception is excluded according to the equations of dynamics), but a change of lengths is quite impossible.

* B. Riemann, "Ueber die Hypothesen welche der Geometrie zu Grunde liegen," *Abh. d. König. Ges. zu Göttingen*, xiii., I. § 1.

III. The Dynamics of a Material Point.

§ 9. *Michelson's Experiment.*

We will now put our general ideas into mathematical form. At the basis of our reasoning we put the following proposition :—

The three-dimensional Euclidean space and one-dimensional time form a unit four-dimensional space-time continuum, in which the time is imaginary.

Laws of motion can be expressed as geometrical properties of such space.

For this purpose we must measure time with the same units as we measure space. Hence, instead of time we take $l=ct$, where c is a velocity.

The velocity c in the above definition is determined from the following proposition :—

In all four-dimensional Euclidean continua, which are relatively in uniform rectilinear motion, there exists one velocity which has the same numerical value for all observers.

As the relative velocity of one system to the other is given by mutual inclination of their time-axes, the problem of finding c is equivalent to the following :—To determine a straight line which is inclined at the same angle to all time-axes of our systems.

We shall for the sake of simplicity use only two dimensions (x, l).

Let this line be (X, L) ; it passes through the origin of coordinates

Let x', l' be the coordinates of any point of this line in the moving system, and x, l in that at rest. Hence

$$x'=x\cos\phi-l\sin\phi\ ;\quad l'=x\sin\phi+l\cos\phi, \qquad (1)$$

where $$\phi=\overset{\frown}{l,\ l'}=\overset{\frown}{x,\ x'}.$$

Hence the velocity of the point is

$$\frac{x'}{l'}=\frac{\frac{x}{l}\cos\phi-\sin\phi}{\frac{x}{l}\sin\phi+\cos\phi}, \qquad (2)$$

Putting $\frac{x'}{l'}=\frac{x}{l}=c=\text{const.}$, it easily follows that $c^2=-1$, and $c=\pm\sqrt{-1}$; but as l is imaginary this velocity will be real.

It is independent of the angle ϕ, and is therefore the same for all systems. There is only one such velocity satisfying this condition.

Experimentally the velocity of light is found to satisfy this condition, and therefore $c =$ velocity of light.

The Lorentz transformations are derived from (1) by inserting the conditions that for the origin $x' = 0$, $x = vt$, and taking real time $it = l$ instead of imaginary.

§ 10. *The first group of equations of motion.*

The motion of a material point is given by its four-dimensional track and not by its projection upon space. Its dynamics is defined by an invariant property of this track: namely the radius of curvature.

For the sake of simplicity we use only three dimensions: two of space and one of time. Let $\frac{1}{\rho}$ be the curvature of the four-dimensional track, and F the force which produces the motion. We will take as the fundamental equation of the dynamics of a material point

$$m \cdot \frac{1}{\rho} = \mathrm{F}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where m, a coefficient of proportionality, is defined as the mass, and accordingly

$$\frac{1}{\rho} = \frac{\sqrt{(dyd^2l - dld^2y)^2 + (dld^2x - dxd^2l)^2 + (dxd^2y - dyd^2x)^2}}{(dx^2 + dy^2 + dl^2)^{3/2}} \cdot \quad . \quad . \quad . \quad . \quad (4)$$

Consider two particular cases:—

i. The point is moving only along the axis of X.

Taking l as the independent variable,

$$\frac{1}{\rho} = \frac{dld^2x}{(dx^2 + dl^2)^{3/2}} = \frac{dl^3}{(dx^2 + dl^2))^{3/2}} \cdot \frac{d^2x}{dl^2} \cdot$$

Hence, if $l = it$,

$$\frac{1}{\rho} = \frac{1}{(\sqrt{1 - v^2})^3} \frac{d^2x}{dl^2},$$

and the equation of motion is

$$\frac{m}{(1 - v^2)^{3/2}} \frac{d^2x}{dt^2} = \mathrm{X}'. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

ii. The point initially moves with constant speed along the axis of X, but under the influence of a force acquires a motion parallel to Y.

$$d^2l=0, \quad d^2x=0, \quad dy=0.$$

$$\frac{1}{\rho}=\frac{\sqrt{dl^2+dx^2}\,.\,d^2y}{(dx^2+dl^2)^{3/2}}=\frac{d^2y}{dl^2}\frac{dl^2}{dx^2+dy^2},$$

or, introducing the real time,

$$\frac{m}{1-v^2}\frac{d^2y}{dt^2}=Y'. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The equations (5) and (6) are identical with the equations of motion derived by A. Einstein in his fundamental paper *: m is the invariant mass.

From these formulas follow two important consequences:

1. *The accelerations of classical mechanics* $\left(\frac{d^2x}{dt^2}, \frac{d^2y}{dt^2}\ldots\right)$ *do not represent an invariant property of motion.*

2. *The mass must be considered as unaffected by the motion.*

We note here that X′, Y′ correspond to the forces as measured from the system moving with the point.

§ 11. *The second group of equations of motion.*

Let the material point move in the four-dimensional continuum. The curvature of its track is given by the equation

$$\frac{1}{\rho}=\frac{d\alpha}{d\tau}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where $d\alpha$ is the angle of contact.

We take a system of coordinates which lies in the osculating plane; then the curve in the neighbourhood of this point can be considered as plane. We have

$$\cos\alpha=\frac{ds}{d\tau},$$

where $ds^2=dx^2+dy^2+dz^2$, and hence from (7)

$$\frac{1}{\rho}=-\frac{d}{dl}\left(\frac{ds}{d\tau}\right). \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

* *Ann. d. Phys.* xvii. § 16 (1905).

We can also calculate the curvature starting from the formula

$$\sin \alpha = \frac{dl}{d\tau};$$

then

$$\frac{1}{\rho} = \frac{d}{ds}\left(\frac{dl}{d\tau}\right). \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

As the motion is characterized not only by the numerical value of the curvature but also by its direction, we introduce the projections of $\frac{1}{\rho}$ upon the axes of coordinates. They are from (8), (9) :

$$\left(\frac{1}{\rho}\right)_\rho = \frac{d}{d\tau}\left(\frac{ds}{d\tau}\right),$$

$$\left(\frac{1}{\rho}\right)_l = \frac{d}{d\tau}\left(\frac{dl}{d\tau}\right);$$

or the equations of motion in four dimensions:

$$\left.\begin{aligned} m\frac{d}{d\tau}\left(\frac{dx}{d\tau}\right) &= \mathrm{R}_x; \qquad m\frac{d}{dt}\left(\frac{dz}{d\tau}\right) = \mathrm{R}_z; \\ m\frac{d}{d\tau}\left(\frac{dy}{d\tau}\right) &= \mathrm{R}_y; \qquad m\frac{d}{dx}\left(\frac{dl}{d\tau}\right) = \mathrm{R}_l. \end{aligned}\right\} \quad . \quad . \quad (10)$$

They coincide with Minkowsky's equations given in his papers *.

Using these formulas, we must sum up the four projections in order to find out the curvature and the force.

If we want the equations of motion in a form representing the force as well as the curvature by its space projections, we must, however, take the equations :

$$\left.\begin{aligned} m\frac{d}{dl}\left(\frac{dx}{d\tau}\right) &= \mathrm{X}; \qquad m\frac{d}{dl}\left(\frac{dz}{d\tau}\right) = \mathrm{Z}; \\ m\frac{d}{dl}\left(\frac{dy}{d\tau}\right) &= \mathrm{Y}; \qquad m\frac{d}{dl}\left(\frac{dl}{d\tau}\right) = \mathrm{L}. \end{aligned}\right\} \quad . \quad . \quad (11)$$

From these there follows the law of momentum accepted in the theory of relativity.

We note particularly that X, Y, Z, L are the forces measured from the system at rest.

* "Grundegleichungen für die elektromagnetische Vorgänge bewegten Körpern," § 14.

§ 12. *The Transformation of Forces.*

Comparing (5), (6), and (11), we obtain the "Transformation of Forces" from a moving system to one at rest.

From (11) we have

$$\frac{d}{dt}\left(\frac{m}{\sqrt{1-v^2}}\frac{dx}{dt}\right)=\frac{m}{(1-v^2)^{3/2}}\frac{d^2x}{dt^2},$$

$$\frac{d}{dt}\left(\frac{m}{\sqrt{1-v^2}}\frac{dy}{dt}\right)=\frac{m}{(1-v^2)^{1/2}}\frac{d^2y}{dt^2};$$

thence the equations of motion become

$$\left.\begin{aligned}\frac{m}{(1-v^2)^{3/2}}\frac{d^2x}{dt^2}&=\mathrm{X},\\ \frac{m}{(1-v^2)^{1/2}}\frac{d^2y}{dt^2}&=\mathrm{Y}.\end{aligned}\right\}\quad\ldots\quad(12)$$

Comparing with (5) and (6), we obtain

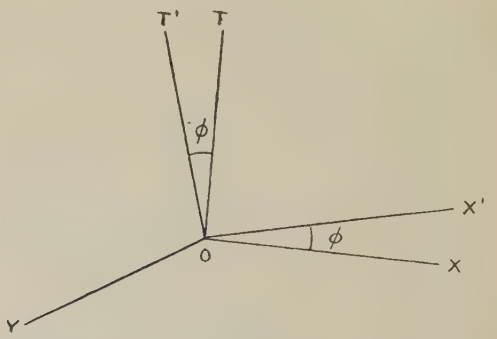
$$\mathrm{X}=\mathrm{X}',\qquad \mathrm{Y}=\sqrt{1-v^2}\,\mathrm{Y}'.\quad\ldots\quad(13)$$

§ 13. *Geometrical interpretation of the Transformation of Forces.*

Our reasoning will be based on two principles:—

1. The motion of a system of reference is characterized by the direction of its axis of time.

Fig. 3.



2. The motion of a material point in space is characterized by a surface in a four-dimensional space-time continuum.

For the sake of simplicity we use only three dimensions.

The motion of a material point at every moment in the system X, Y, Z, where X, Y is space and T is time, is determined by the section of this surface by X, Y, T.

Let us have a system of reference at rest X, Y, T, and a system moving in the direction of X : X′, Y′, Z′. The plane T′OX′ coincides with TOX, the axis OY′ with OY, and the angle ϕ is defined by

$$\cos(\widehat{x, x'}) = \cos(\widehat{l, l}) = \frac{1}{\sqrt{1-v^2}}.$$

The motion of a material point at O is given by a surface tangent to the plane X′OY at the point O. OT′ will be normal to this surface.

Now we can find the Transformations of Forces from the system at rest to the moving system.

1. *Direction of* X.—In the stationary system XOT the motion is given by the section of our surface by the plane XOT; in the moving system by the plane X′OT′. As these two planes coincide, the two curves of intersection will be identical; hence X′ = X.

2. *Direction of* Y.—In the stationary system the motion will be given by the section TOY, which is an oblique one; in the moving system by the section T′OY, which is a normal one, as it contains the normal OT′. Hence, according to the well-known theorem of Meunier,

$$(\rho)_{T'OY} \cos\phi = (\rho)_{TOY}$$

or $$Y\cos\phi = Y' \text{ and } Y = \sqrt{1-v^2}\, Y'.$$

By the same train of reasoning we can also explain the asymmetry of the laws of motion.

§ 14. *The Law of Energy.*

According to the laws of motion the force is normal to the track; hence

$$X dx + Y dy + Z dz + L dl = 0. \quad . \quad . \quad . \quad (14)$$

This gives us the meaning of L; *i.e.* the work done by the forces in unit of time. If we use the real coordinate of time, and c is the velocity of light, the vector X, Y, Z, L coincides with the force vector of Electrodynamics,

$$\mathbf{F}, \frac{i}{c}(q, \mathbf{F}),$$

where **F** is the vector of force and q the velocity.

The fourth equation of (10) and (11) gives us the law of energy.

§ 15. *Hamilton's Principle.*

The problem of determining the motion of a material point under the influence of the force X, Y, Z, L is the same as finding the geodesic line between two points $x_1y_1z_1l_1$ and $x_2y_2z_2l_2$:

$$\delta\int_{l_1}^{l_2} d\tau=0$$

under the condition that it must be normal to the vector X, Y, Z, L.

If the force is derived from a potential so that $X=\frac{\partial\psi}{\partial x}$, $Y=\frac{\partial\psi}{\partial y}$ etc., the problem reduces to that of finding the geodesic line of the surface $\psi=0$ between two fixed points.

We have

$$\delta\int_{l_1}^{l_2} d\tau=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

$$\psi=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Hence

$$\delta\int_{l_1}^{l_2} d\tau+\lambda\psi dl=0. \quad . \quad . \quad . \quad . \quad . \quad (17)$$

By an easy calculation we derive, remembering that the end points are fixed,

$$\int_{l_1}^{l_2}\Big(-\frac{d}{dl}\frac{dx}{d\tau}+\lambda\frac{\partial\psi}{\partial x}\Big)\delta x+\Big(-\frac{d}{dl}\frac{dy}{d\tau}+\lambda\frac{\partial\psi}{\partial y}\Big)\delta y$$
$$+\Big(-\frac{d}{dl}\frac{dz}{d\tau}+\lambda\frac{\partial\psi}{\partial z}\Big)\delta z+\Big(-\frac{d}{dl}\frac{dl}{d\tau}+\lambda\frac{\partial\psi}{\partial l}\Big)\delta l=0.$$

Hence, making the coefficients of the variations δx, δy, δz, δl vanish, we derive the equations of motion (11), where $\lambda=\frac{1}{m}$.

The general form of the law of motion will then be

$$\delta\int_{l_1}^{l_2}(md\tau+\psi dl)=0, \quad . \quad . \quad . \quad . \quad (18)$$

or

$$\delta\int_{l_1}^{l_2}(m\sqrt{1-v^2}+\psi)dl=0. \quad . \quad . \quad (19$$

It follows, therefore, that *neither the Lorentz transformations nor four-dimensional geometry can give us the properties of matter, but merely the laws of motion.*

IV. Non-Euclidean Space.

§ 16. *The metric of a space, and the physical properties of solid bodies.*

The generally-accepted conception in classical physics and in geometry was that the metric of a space is a property inherent in the space itself. Geometry bore no necessary relation to the physical properties of phenomena which we utilize in measuring the distance between two points. A breach in this conception was made by Einstein in his special theory of relativity. If the measured body and the observer are in relative motion, no other way of measurement is possible than by light-signals; and it appeared that a particular property of light-propagation (the constancy of velocity) has a decisive influence upon the metric of a space.

That the metric of a space must be considered in connexion with the physical properties of solid bodies and light was emphasized before Einstein by Riemann.

Thus, considering the metric of infinitely small parts of space, he says * :—

"Nun scheinen aber die empirischen Begriffe in welchen die räumlichen Massbestimmungen gegründet sind, der Begriff des festen Körpers und des Lichtstrahls, im unendlichkleinen ihre Gültigkeit zu verlieren; es is also sehr wohl denkbar, dass die Massverhältnisse des Raumes im Unendlichkleinen den Voraussetzungen der Geometrie nicht gemäss sind, und dies würde man in der That annehmen müssen, sobald sich dadurch die Erscheinungen auf einfachere Weise erklären liessen."

We take also as our starting-point these ideas of Riemann and Einstein, and try to find what metric is compatible with the laws of solid bodies and light.

As at the basis of every metric of space lies the conception of a distance between two points, we define it strictly as :

The measured distance or interval between two points is a number which we receive as a result of measurement by some physical phenomenon, if we introduce afterwards the necessary corrections which exclude the influence of this particular kind of phenomenon (the temperature, pressure, etc.) upon our result.

* B. Riemann, *ibid.* p. 149.

§ 17. *Geometrical forms and physical bodies in a curved space, and their projection upon Euclidean space.*

Let us consider how any geometrical form and a physical body in a curved space will be projected for an observer in Euclidean space, assuming that he carries out all measurements by light-signals.

Let us have in a curved space a straight geometric line AB (in Euclid's sense). It is clear that its projection upon Euclidean space will be shortened and curved. The length and the form of this projection can be found from the formulas of the Theory of Relativity.

Quite different is the behaviour of an elastic body in a curved space. For this purpose we take into account also the accelerations.

We assume now that in the previous example AB is an elastic cylindrical rod, and find its projection upon Euclidean space.

It will undergo the FitzGerald "contraction," which is the same for all bodies, and does not depend on their material ; it will also suffer elastic deformations under the influence of the accelerations, according to the laws of Elasticity ; and these deformations in contradistinction to the first will not be the same for all bodies, but will depend on the special elastic properties of the body. But for elastic bodies, as easy calculations show, the first "contraction" (FitzGerald's) is much smaller than the second effect, and can be neglected ; so that the shape and sizes of bodies can be found by taking into account only their elastic deformations.

§ 18. *The theorem about the metric of a curved space.*

A curved space has no universal metric: that is to say, its metrical properties depend upon the material of the gauges and the kind and place of measurement.

Proof.— Let us have in Euclidean space an elastic body of some material and shape, and let us find its shape in a curved space.

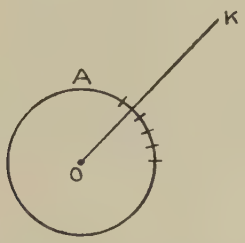
(1) We can consider a curved space as a field of force in Euclidean space, and thus find the form of our body, applying the formulas of relativity and elasticity. According to the above its shape will be a function of its elastic properties, and will not be the same for different materials.

(2) Suppose that a curved space has a universal metric; that is to say, the measured distance between two points does not depend upon the kind of measurement. Then two material

rods of the same length and shape in Euclidean space, but of different material, must have also the same length and shape if transferred in non-Euclidean space. But this is contrary to our previous conclusion.

An example will make the matter clearer. Let us investigate the metric of a uniformly rotating space. We shall see that the ratio s/d, where s is the length of the circumference and d the diameter, will have no definite value. We can regard the space near O as Euclidean, and assume that all our gauges will be taken from O.

Fig. 4.



1. Let us have an absolutely rigid gauge of a unit length (at O), and find the length of A. Suppose that s such gauges placed one next to the other give us the length of A, and r such gauges the length of R.

Now, the length of such a gauge measured at the circumference A will remain 1, because there is no "relativity" correction, as the body and the observer have no relative velocity. Along the radius we have also no "relativity" correction, and as the gauge is an absolutely rigid body also no elastic deformations. Therefore it is clear that the length of the circumference will be in our case $s = 2\pi R$, the same as in Euclidean space.

2. We can now measure all the s gauges at A from O by light-signals. But as from this point every gauge will become shortened (because the observer and the gauge are in relative motion), the length of A will be $2\pi R\sqrt{1-v^2}$; that is $s/R < 2\pi$.

3. The length of the gauge will, if measured by light-signals, be a function of the position of the observer, and will not be the same for all observers along OK, as their velocities relative to the gauges will be different.

4. If we measure the length of the radius by an elastic gauge, then it will be deformed by the centrifugal force; the deformation will be very considerable, and not the same

for every material ; and if we measure the radius by two gauges which are equal at some part of our space but composed of different material, we shall obtain different results for the ratio s/R.

5. The following example relates to *time-measurement*. Let us measure time on a planet, a uniform homogeneous sphere. We take two similar clocks, make them synchronous in one part of space and afterwards transport one of them to another part. Now we can measure the time in any one of these two parts of space either by its respective clock or by means of a signal from the clock of the other part. If the planet does not rotate, the two results will be different at points at unequal distances from the centre, but they will be the same on the surface of the planet. If the latter rotates, then it is clear that even on the surface these results for the Pole and the Equator will not agree.

Hence the space of gravitation and rotation are non-Euclidean.

CXXXIV. *Specific Heat Variations in Relation to the Dynamic Action of Gases and their Equations of State.* By Wm. J. Walker, *University College, Dundee* *.

[Plate XXXVI.]

Summary.—Some preliminary experiments are first described relating to the determination of the variable specific heat function for highly superheated steam. It is emphasized that the neglect of any explicit incorporation of such a function in the thermodynamic equations for vapours obscures the reasons for many otherwise apparently anomalous results. The experimental data so far obtained are few, owing to difficulties encountered in the experimental method, but they indicate the probable existence of an inflexion point on the constant-pressure specific heat-temperature curve at the critical temperature. An analytical investigation into the problem of incorporating the variable specific heat function into the equations of state for gases and vapours occupies the latter portion of the paper. By a combination of fundamental thermodynamic relations with the most probable adiabatic relation for gases and vapours, as revealed by experiment, an equation of the Dieterici-Jeans type has been derived, the qualitative agreement of which with the behaviour of gases and vapours in general appears to be good. By its form, the evidence also appears to be strong that the partial disagreement of this and other earlier types

* Communicated by the Author.

of equation with the physical constants of gases and vapours is due to the absence of any term in such equations directly involving specific heat variations.

THE difficulty of measuring directly the specific heats K or K_v of gases or vapours is well recognized and has led to the development of several indirect methods which depend, either wholly or partially, on the effects of the specific heats on the external dynamic actions of a gas or vapour. The experimental difficulties of most methods, direct or indirect, are in no way diminished by the fact that the specific heats vary continuously with temperature or pressure or both. In practically all methods, indeed, with the apparent exception of one, the specific heat values obtained are actually mean values between the pressure and temperature limits involved, and the problem of determining the specific heats at particular points such as those close to saturation becomes extremely difficult. The one method which is comparatively free from the effect of such variations is the velocity of sound method, developed and applied so successfully in recent years by Prof. Dixon and others, and on which, no doubt, reliance will be placed in the future for the acquisition of the most accurate data.

It is the purpose of this paper to describe first some preliminary experiments, carried out with the object of arriving at the specific heat variations of highly superheated steam by the application of equations involving the effect of such specific heat variations on gas discharges and velocities through orifices or nozzles. This method, the fundamental theory of which has been given in two previous papers *, suffers to some extent from the disadvantage of giving mean values only, but the pressure and temperature limits between which such values are obtained may, by virtue of the method, be made sufficiently narrow to compensate materially for this. It is desired also to introduce a new point of view into the treatment of adiabatic changes of state and their relation to other thermodynamic factors, which treatment has resulted in the derivation of a new equation of condition for gases and vapours. The fact that this equation continues the line of development from the equations of van der Waals, Dieterici, and Jeans, and also

* "The Effect of Variable Specific Heat on Gas Discharges," Phil. Mag. (March 1922); "The Critical Pressure Ratio of Gases," Phil. Mag. (October 1924).

that it has been derived from the conjunction of a closely approximate and apparently widely applicable experimental fact with orthodox thermodynamic theory, are considered sound enough excuses for adding yet another to the long list of such equations.

The pronounced effect of variable specific heat on the thermodynamic efficiencies of internal combustion engines has been recognized for some appreciable time, and in a previous paper * the writer has shown that by a suitable and close approximation the resulting equations for thermodynamic efficiency are in no way seriously complicated by such specific heat variations, and they can readily be applied in the ordinary analytical work involved in drawing up heat balance sheets. In view of this recognized effect of variable specific heat on thermodynamic efficiency, students of heat engine theory cannot but be struck by the absence of any explicit incorporation of a factor or factors expressing such specific heat variations in the usual analysis as applied to steam-engine or steam-turbine theory. It is well known that the specific heat of steam varies widely, both with temperature and pressure, but any attempt to incorporate the effect of variable specific heat on thermodynamic efficiency does not appear to have been made. The reason lies, no doubt, in the impression that the analytical work would become so involved as to make the attempt scarcely worth while. In internal combustion engine theory, reliance can be placed on the ordinary ideal equation of condition for gases, and the interposition of factors involving variable specific heat effects introduces but little extra complication. In the case of vapour engines, however, the thermodynamic equations are, in general, already so complicated that it is considered advisable to fight shy of the introduction of further variable factors.

It is admitted, of course, that the drawing up and use of steam or other vapour tables will always be necessary to facilitate ready calculation, and that these tables do implicitly incorporate the effects of specific heat variations, whether correctly or not, and will give results the reliability of which will be in proportion to the accuracy of the tables used. The point which it is desired to make here, however, is that the direct inclusion, in analysis, to a sufficiently approximate degree, of some factor or factors which determine specific heat variations, may throw valuable light on

* "Thermodynamic Cycles as affected by Variable Specific Heat," Phil. Mag. (Sept. 1917).

many otherwise anomalous results. It can, perhaps, be fairly claimed that the inclusion of such factors in the analysis of the flow of gases and vapours through nozzles does result in the derivation of closely approximate equations which obviously lend themselves to experimental study of the direct effects of specific heat variations. As has already been shown *, the difference between the effects produced by variable specific heat on the velocity and on the quantity of steam discharged is not one of *magnitude* only but also of *sign*—a fact sufficiently important and striking, perhaps, to call for more emphasis than usual, particularly when it has received important experimental verification †.

The apparatus for use in the preliminary experimental investigation into the flow of highly superheated steam through nozzles is shown in Pl. XXXVI. Two cast-iron boxes, A and B, of square section and 6 in. internal dimension, are shown bolted together with the nozzle plate between. The temperature of the steam is measured by a calibrated iron-constantan couple placed just behind the nozzle plate and opposite the centre of the nozzle orifice. The pressure was measured by a Bourdon gauge, calibrated against a dead-weight tester. It is admitted that this pressure-measurement method is not entirely satisfactory, and it is intended to substitute for it a more reliable mercury-manometer method in later work; but great care was exercised in its use, and, in view of the preliminary nature of the work, it is considered to have given fairly accurate service. The main object of this preliminary work was to determine the best means of obtaining high superheats.

In box A, a specially designed direct current electric heater is inserted, made of nickel-chrome wire wound over built-up mica elements. The steam, which passes from valve V and is already superheated to some degree in an ordinary fire superheater, is then raised further in temperature by this electric heating device. By this means, and by carrying as many heating elements as possible inside the box up to half its length, temperatures in the neighbourhood of 700° C. abs. have been obtained over a sufficiently long period to enable satisfactory tests to be made. It has been found, however, that after a period of steam heating in this way, the wire deteriorates and fuses even when well within its current-carrying capacity. This fact has so

* Phil. Mag. (Oct. 1924) pp. 706–707.
† *Ibid.*

seriously impeded the progress of the tests, that arrangements are now being made for the incorporation of more rigid alternating current heating elements, with which it is hoped to secure more rapid and continuous working. One experimental point worth noting about such heaters is that it appears to be impossible to start them in operation with the valve V open and steam passing. Even although the electric current is just switched on immediately after opening the valve, fusing always occurs at once, and the reason was found to lie in the formation of thin films of moisture over and between the layers of mica. This was evidenced by the swollen appearance of the mica elements, on opening up the box to repair the fault. The heater must therefore always be in operation before valve V is opened for the passage of steam, and under such conditions of working no swelling of the mica takes place. It is clearly a great advantage to have naked wire heaters for such work in order to derive maximum heating effect, and if attention is given to the foregoing possible source of trouble there appears to be no other obstacle to their use for steam heating.

On issuing from the nozzle, the steam passes through box B into the tapered pipe T, whence it is conducted to a surface condenser, where it is collected and weighed. The box B was originally fitted with a specially prepared heat-resisting glass window, the object being to photograph the jet in order to obtain data relating to its coefficient of contraction. Difficulty has been experienced, however, in obtaining sufficiently clear glass to withstand the high temperatures, and the glass window was replaced later by a sheet-iron plate. It is hoped, however, to surmount this difficulty and revert to the photographic work at a later stage.

Several types of nozzle were tried out in the earlier experiments, including both sharp-edged and streamlined forms, and the nozzle finally chosen for the investigation was one of streamlined form, 0·518 in. diameter and 0·5 in. long, made of brass and screwed firmly into the nozzle plate. The nozzle has most probably a coefficient of discharge which is practically unity under all conditions of pressure and temperature, and the quantity of steam which it discharges above the critical pressure ratio was of the best order to minimize any possible errors due to collection in the condenser plant. Thus, smaller discharges required lengthier operation for each test in order to obtain a good average discharge, and so involved risk in pressure and temperature changes. Also, any greater discharge resulted

in higher condenser temperatures with increased risk of deficient collection of the discharge due to evaporation. Any risk of this was minimized to a great extent in the actual tests by discharging into a practically closed vessel.

In all, some thirty to forty tests were completed, but of these only seventeen were made with the $\frac{1}{2}$ in. streamlined nozzle before it was found necessary to alter the design of heater. The results are given herewith in Table I. The pressures and temperatures on the upstream side were p_1 and T_1, those on the downstream side not being given, since they were in each case well below the value defined by the critical ratio. In the first nine tests with this nozzle the practice was adopted of reading the pressure at frequent intervals after adjustment of the valve V, without in any way attempting to maintain a closely constant value. It was found, however, that at the higher pressures the fluctuations due to boiler pressure changes were too pronounced to be allowable for accurate work, since the specific heat changes which occur with pressure changes are appreciable. Hence, in the last eight recorded tests the pressure was maintained practically constant by hand regulation throughout each test.

The specific volume V_1 of the steam is calculated from Callendar's equation,

$$V_1 = 1{\cdot}0706\frac{T_1}{p_1} - \left\{\frac{157{\cdot}2\times 10^6}{T_1^{10/3}} - {\cdot}016\right\} \text{ cu. ft.}$$

The quantity Q_a is the actual discharge in lb. per second, while Q_t is the corresponding theoretical discharge given by

$$Q_t = {\cdot}668\sqrt{p_1/V_1},$$

which is calculated, following Callendar, by taking the adiabatic index as 1·3. If, however, the true adiabatic relation between pressure, volume, and temperature is given by

$$pV^m e^{\lambda T} = \text{constant}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

the actual discharge equation will be

$$Q_a = Q_t\left\{1 - \frac{3}{4}\frac{\lambda T_1}{m}\left(1 - x^{\frac{m-1}{m}}\right)\right.$$

to a first and close approximation,

$$\text{whence} \qquad \lambda = \frac{Q_t - Q_a}{{\cdot}577\, T_1(1 - x^{\cdot 231})Q}.$$

For the critical value of x the pressure ratio, and again taking $m = 1{\cdot}3$, this gives

$$\lambda = \frac{Q_t - Q_a}{{\cdot}0752\, T_1 Q_t}.$$

Values of λ so calculated are given in the seventh column, and it is necessary to note first their precise significance. As obtained, λ is a term derived from a combination of Prof. Callendar's and the writer's equations, and its value in all cases will depend on the validity of either or both of these sets of equations. Prof. Callendar has built up his theory on the assumption of an adiabatic equation of the form pV^m = constant, and for current practical steam pressures and temperatures there is no doubt that his tabular data so derived are sufficiently accurate. It is generally accepted, however, that (1) is nearer the true type of adiabatic equation in general for all gases. The unimportance of the term λT in dealing with steam has not necessarily arisen because of the smallness of λ or similar function, but because of the relatively much lower values of T in steam engine as compared with internal combustion engine operation. Prof. Callendar *, however, considers (1) or any adiabatic equation explicitly involving a variable specific heat factor as too complicated for practical purposes or as a standard of reference. The verification of the reversal effect † by the recent tests of the Steam Nozzles Research Committee of the Institution of Mechanical Engineers and given in their Third Report [1924], is good evidence that λ is not a negligible term. In the Fourth Report ‡ [1925], however, it is stated that the velocity curves for all superheats, with one exception, fall within the experimental band defined by errors of observation, etc. This, however, in no way invalidates the writer's deductions from the Committee's tests, for it is important to note that the band comprised between the experimental discharge curves at low and high superheats is of three times the average extent of the velocity band. Not only so, but since the quantity band has a reversed tendency to that of the velocity band, it will be necessary to postulate six times the probability of error in quantity measurement over that allowed in velocity measurement if the writer's deductions

* Proc. I. M. E. (March 1924), p. 377.
† Phil. Mag. (Oct. 1924).
‡ Proc. I. M. E. (May 1925).

are to be wholly invalidated. No reference is made in the Fourth Report to these quantity measurements. The experiments, indeed, emphasize the fact that λ is a term highly sensitive to experimental detection when fairly accurate measurements of both velocity and quantity are made, and it would appear worth while, therefore, to explore its value.

TABLE I.

p_1. lb. per sq. in abs.	T_1. °C. abs.	V_1. cubic feet.	Q_t. lb. per sec.	Q_a. lb. per sec.	C_d.	λ.
25·99	481·0	19·64	·0770	·0788	1·023	−·000648
25·89	485·0	19·90	·0763	·0778	1·020	−·000540
26·01	513·6	21·01	·0745	·0755	1·013	−·000347
26·22	547·5	22·28	·0727	·0734	1·009	−·000124
29·02	559·9	22·94	·0715	·0713	0·998	+·0000665
67·60	586·5	9·20	·1809	·1808	1·000	+·0000125
65·30	579·0	9·36	·1765	·1783	1·010	−·000234
67·18	627·7	9·94	·1740	·1760	1·011	−·000244
66·78	653·9	10·43	·1691	·1689	·99	+·0000240
56·00	515·8	9·72	·1605	·1619	1·007	−·000225
56·00	552·2	10·46	·1549	·1534	·992	+·000233
56·00	581·4	11·02	·1507	·1501	·996	+·0000910
56·00	615·4	11·70	·1462	·1437	·983	+·000370
56·00	648·2	12·35	·1425	·1375	·965	+·000720
56·00	680·6	12·96	·1390	·1353	·974	+·000521
56·00	698·0	13·32	·1375	·1372	·998	+·0000416
56·00	708·5	13·50	·1362	·1372	1·007	−·000138

Referring now to Table I., the sixth column of which gives values of C_d the coefficient of discharge, one may say that, in general, their close approximation to unity is, to a large extent, justification of the practical value of Callendar's equations at moderate pressures. The variations in its value with temperature, however, are sufficiently wide to merit examination, but it is better to do this with reference to the values of λ. Referring now to the last eight tests in which the pressure was maintained constant throughout. it appears that λ first increases and then diminishes, the maximum point being reached in the neighbourhood of the critical temperature of 647° C. abs. This indicates the presence of a point of inflexion at the critical temperature on a constant pressure curve, showing the relation between K_p and T. In the tests at a pressure of approximately 26 lb. per sq. in. the critical temperature was never reached, but there again

the results show a tendency for λ to increase in value from negative to positive as the temperature is increased up to the critical temperature. In the case of the four tests at 65 to 67 lb. per sq. in. the fluctuations in pressure which occurred were too great to render the results of sufficient accuracy to be reliable, and it was these tests, in fact, which revealed the imperative necessity of maintaining constancy of pressure throughout each test, as was done later at the 56 lb. pressure. It should be noted, of course, that these values of λ are not absolute values, but values relative only to the joint validity of Callendar's and the writer's equations. If both are correct, λ should be zero and both sets of equations become identical. In any case, such relative values of λ are useful as indications of the relative changes of specific heat which may occur at different temperatures and pressures. The question of determining absolute values of λ will be the subject of later reference. It is interesting, however, to compare the values of λ obtained here in relation to the value $+\cdot000283$, which represents a fairly average value for the gaseous mixture of an internal combustion engine. At the high temperatures common to such engines this value has a far-reaching effect upon efficiency, but at ordinary steam-engine pressures and temperatures the effect of values such as those tabulated here would be small and practically negligible.

It is admittedly a somewhat optimistic procedure to look for much accuracy in the determination of a quantity of such small order in relation to the other quantities measured. Repeated tests, however, always showed excellent consistency in the determination of values of Q_a. In many cases Q_a was repeatedly obtained over several intervals, each occupying about ten minutes, and the variation in discharge under constant temperature and pressure conditions was always less than 0·5 per cent. Friction effects have been neglected, and, in view of the short convergent streamlined nozzle used, these must in any case have been small. They certainly do not account for the variations observed.

The experiments just described are, however, but preliminary ones, and are given here only while awaiting the opportunity to recommence tests on wider scales of both pressure and temperature. Concurrently with the experimental work, analytical investigations have been made into the possibility of including the variable specific heat factor or factors into the equation of state for vapours. As some measure of success appears to have been obtained in this

direction, it is perhaps not out of place to give the results here at the same time.

It is appreciated, of course, that the foregoing method offers several points apparently open to criticism. Thus, it might be objected that the specific heats of gases and vapours vary with pressure as well as temperature, and so apparently the analysis becomes unsound for practical application, since it contains no term explicitly involving specific heat variation with pressure. It is quite possible, however, for a gas or vapour, provided it possesses the requisite properties, to expand adiabatically according to a law analytically expressed by formulæ of the type

$$\left.\begin{aligned} \text{and} \qquad & \mathrm{T}V^{m-1}e^{f(\mathrm{T})} = \text{constant} \\ & \mathrm{P}^{1-m}\mathrm{T}^{m}e^{f(\mathrm{T})} = \text{constant} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

It is necessary only to assume that such adiabatic relations hold (and it must be admitted that the experimental evidence for equations of such general form is strong) and proceed therefrom to develop, if possible, the other thermodynamic relations and so determine whether or not the required properties approximate at all to the required properties of gases and vapours. This is the method applied by Callendar in the derivation of his own equations. This assumption also meets another possible criticism which might be raised, to the effect that λ is not a constant term. The assumption of any function $f(\mathrm{T})$ instead of $\lambda\mathrm{T}$ as the hyperbolic index makes no difference to any of the analysis already developed by the writer in previous papers. Provided $f(\mathrm{T})$ is considered as an algebraic function having constant coefficients of relatively low value attached to powers of T, the first approximation equations will remain as before except that the term $\mathrm{T}f'(\mathrm{T})$ will replace $\lambda\mathrm{T}$ wherever it occurs, $f'(\mathrm{T})$ being the first differential coefficient of $f(\mathrm{T})$. That the coefficients are low enough to make this approximation sufficiently close to be of value in analysing experimental data, can scarcely be disputed. Thus the discharge and velocity formulæ, given in previous papers, will become

$$\mathrm{Q}_a = \mathrm{Q}_t \left\{ 1 - 3\mathrm{T}f'(\mathrm{T}) \frac{1 - x^{m-1}}{4m} \right\}$$

and

$$u_a = u_t \left\{ 1 + \mathrm{T}f'(\mathrm{T}) \frac{1 - x^{m-1}}{4m} \right\}$$

as first approximations.

From (2)

$$T^m e^{f(T)} = C_1 P^{m-1}$$

and

$$T e^{f(T)} = C_2 V^{1-m},$$

where C_1 and C_2 are constants.

By differentiating, these equations give respectively

$$\frac{dP}{P} = \frac{m + Tf'(T)}{m-1} \cdot \frac{dT}{T} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and

$$\frac{dV}{V} = \frac{1 + Tf'(T)}{1-m} \cdot \frac{dT}{T} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

In an adiabatic process, however,

$$K_P dT = T\left(\frac{dV}{dT}\right)_P dP \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and

$$K_V dT = -T\left(\frac{dP}{dT}\right)_V dV. \quad . \quad . \quad . \quad . \quad (6)$$

Also, since

$$K_P - K_V = T\left(\frac{dP}{dT}\right)_V \left(\frac{dV}{dT}\right)_P, \quad . \quad . \quad . \quad (7)$$

equations (3) to (7) when combined give

$$\frac{1}{m-1}\left\{ P(m + Tf'(T))\left(\frac{dV}{dT}\right)_P - V(1 + Tf'(T))\left(\frac{dP}{dT}\right)_V \right\} = T\left(\frac{dP}{dT}\right)_V \left(\frac{dV}{dT}\right)_P.$$

$$\therefore \quad \frac{1}{m-1}\left\{ (m + Tf'(T))P\left(\frac{dT}{dP}\right)_V - (1 + Tf'(T))V\left(\frac{dT}{dV}\right)_P \right\} = T.$$

Solving for this differential equation gives

$$\frac{(m-1)dP}{\{m + Tf'(T)\}P} = -\frac{(m'-1)dV}{\{1 + Tf'(T)\}V} = \frac{dT}{T},$$

the most general solution of which is given by

$$\frac{PV}{T} = F\{TV^{m-1}e^{f(T)}\}, \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where F denotes some undetermined function. Before arriving tentatively at the most probable form of this function F, it will be assumed, following other investigators, that the volume V of a gas or vapour is more approximately expressed by $V-b$, where b is the well-known "co-volume" of the molecules. Following the form of equation initially proposed by Dieterici and supported by Jeans's theory, a probable form of (8) is given by

$$P(V-b)=RTe^{-\frac{a}{T^N V^M e^{\phi(T)}}}, \quad . \quad . \quad . \quad . \quad (9)$$

where the relation between N, M, and ϕ is such as to satisfy that between 1, $m-1$, and f.

Equation (9) clearly follows the general form of the isothermal curves expressing the relation between PV and P for gases and vapours, as do the equations of van der Waals and Dieterici. In order to determine the most probable values of the indices N, M, and ϕ, it is necessary first to inquire into the dependence of the critical temperature, pressure, and volume on these factors.

At the critical point, both $\left(\frac{dP}{dV}\right)_T$ and $\left(\frac{d^2P}{dV^2}\right)_T$ must be zero.

From (9),

$$\left(\frac{dP}{dV}\right)_T=\frac{RTe^{KV^{-M}}\{-KV^{-M-1}M(V-b)-1\}}{(V-b)^2}=0, \quad (10)$$

where

$$K=-\frac{\alpha}{T^N e^{\phi(T)}}. \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Also

$$\left(\frac{d^2P}{dV^2}\right)_T=$$

$$RTe^{KV^{-M}}\Big[\frac{1}{(V-b)^2}\Big(-KMV^{-M-1}\{-KMV^{-M-1}(V-b)-1\}$$

$$-KM(-M-1)V^{-M-2}(V-b)-KMV^{-M-1}\Big)$$

$$-\frac{2}{(V-b)^3}\{-KMV^{-M-1}(V-b)-1\}\Big]=0. \quad . \quad (12)$$

Equations (10) and (12) combined give the equation for

the critical volume V_c as

$$-KM(-M-1)V_c^{-M-2}(V_c-b)-KMV_c^{-M-1}=0,$$

whence
$$V_c=\frac{M+1}{M}b. \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

But, from (10),

$$K=\frac{1}{-MV^{-M-1}(V-b)}.$$

$\therefore$ from (13),

$$K_c=-\left(\frac{M+1}{M}\right)^{M+1}b^M, \quad . \quad . \quad . \quad . \quad (14)$$

so that from (11),

$$T_c e^{\frac{\phi(T_c)}{N}}=\left\{\frac{\alpha}{b^M}\left(\frac{M}{M+1}\right)^{M+1}\right\}^{\frac{1}{N}} \quad . \quad . \quad . \quad . \quad (15)$$

Equations (9), (13), and (15) then combined give

$$P_c e^{\frac{\phi(T_c)}{N}}=\left\{\frac{RM^{M+N+1}\alpha}{b^{M+N}(M+1)^{M+1}}\right\} \quad . \quad . \quad . \quad . \quad (16)$$

It is interesting to note that the critical volume depends only on the values of b and M, while both the critical pressure and temperature depend on the five terms α, b, M, N, and ϕ.

Again, since
$$P_c=\frac{RT_c e^{K_c V_c^{-M}}}{V_c-b},$$

$$\therefore \quad \frac{RT_c}{P_c V_c}=\frac{V_c-b}{V_c e^{K_c V_c^{-M}}}.$$

$\therefore$ from (13) and (14),

$$\frac{RT_c}{P_c V_c}=\frac{e^{\frac{M+1}{M}}}{M+1}. \quad . \quad . \quad . \quad . \quad . \quad (17)$$

The ratio RT_c/P_cV_c, which has been the subject of much experimental study, is therefore dependent only on the value of M. The observations of Young * and others show that the value of this ratio varies for different gases, being about 3·7 in most cases and ranging from below 3·5 to above 4 in others. The inference is, therefore, that M has varying values for different types of gases. Noting now

* Phil. Mag. (Feb. 1892).

that the value of M in (17) should be in the neighbourhood of unity in order to approximate to the above values of the ratio RT_c/P_cV_c and that M is some function of the adiabatic index m, the question arises of adjusting the constants M and N to agree with the adiabatic relation involving m. In the simplest and most obvious form the adjustment may be taken as given by $N=\frac{1}{m-1}$ and $M=1$. Although this immediately disposes of any possibility of variation of the ratio RT_c/P_cV_c it is nevertheless interesting, since it gives the same index value to V as in Dieterici's and Jeans's equations. At the same time it does not necessarily involve disagreement with observations of the cooling effect and saturation pressures as in the case of Dieterici's equation. This can be seen at once by determining the value of $\left(\frac{dP}{dT}\right)_V$, which gives the inverse value of the cooling effect at the critical point.

From (7),

$$P=R''Te^{\psi(T)},$$

where

$$R''=\frac{R}{V-b}$$

and

$$\psi(T)=-\frac{\alpha}{T^N V^M e^{\phi(T)}}.$$

$$\therefore \quad \left(\frac{dP}{dT}\right)_V=R''e^{\psi(T)}\{1+T\psi'(T)\}$$

$$=\frac{P}{T}\{1+T\psi'(T)\}$$

$$=\frac{P}{T}\left[1+\frac{\alpha T^{-N}e^{-\phi(T)}}{V^M}\{n+T\phi'(T)\}\right],$$

which, from (13) and (15), gives

$$\left(\frac{dP}{dT}\right)_V=\frac{P}{T}\left[1+\frac{M+1}{M}\{N+T\phi'(T)\}\right].$$

If $N=\frac{1}{m-1}$ and $M=1$, this gives

$$\left(\frac{dP}{dT}\right)_V=\frac{P}{T}\left[\frac{m+1}{m-1}+\frac{2T}{m-1}f'(T)\right];$$

or, if the slope of the constant pressure specific heat-temperature curve at the critical point is given by λ, this becomes

$$\left(\frac{dP}{dT}\right)_v = \frac{P}{T}\left[\frac{m+1}{m-1} + \frac{2\lambda T}{m-1}\right].$$

In the case of triatomic gases such as steam and carbon dioxide, the value of m according to the Kinetic Theory should be $\frac{4}{3}$, hence

$$\left(\frac{dP}{dT}\right)_v = \frac{P}{T}\{7+6\lambda T\}. \quad . \quad . \quad . \quad . \quad (18)$$

The term λ is here the correction factor required to bring experimental values into line with theory. In the case of CO_2 the approximate value of $\left(\frac{dP}{dT}\right)_v$ is $6{\cdot}5\,\frac{P}{T}$, indicating that at the critical point λ is a small negative term of the order of ·00013. It will be seen, therefore, that it is at least probable that the term λ disposes of the usual difficulty involved in reconciling the constants N and M in order to satisfy observations of the various physical properties of gases and vapours.

The foregoing reasoning applies, whatever the value of M may be. The objection to its having the same value, unity, for all gases lies in the observed variations in the ratio RT_c/P_cV_c. The objection is not a serious one, however, since there are grave difficulties in the accurate experimental determination of V_c. Also, as Callendar has pointed out, Maxwell's theorem on the continuity of state makes no reference to the zero datum for V, so that adjustments to suit experimental observations are usually possible. There is, however, another way, possessing peculiar points of interest of its own, of considering this question. Jeans's equation

$$P(V-b) = RTe^{-\psi/RTV},$$

where ψ is an unknown function depending only on the law of force between the molecules, indicates that the variation in the force between molecules of differently complex structures may be the factor which accounts for the variation of RT_c/P_cV_c. Thus, Jeans has shown * that since the variation of the viscosity K of a gas may be represented by

$$K = K_0\left(\frac{T}{273}\right)^{n'},$$

* 'Dynamical Theory of Gases,' p. 257 (Cambridge Univ. Press, 1904).

where n' is an index which is different for different gases, the average force between two molecules is a function of n'. It is doubtful whether it is possible to arrive at the precise form of the function ψ by reasoning according to the principles of the Kinetic Theory, but it is interesting to note that the values of $n'm$ for the gases, values of n' for which are given by Jeans, are in the neighbourhood of unity throughout. Table II. here gives several of these values.

TABLE II.

Gas.	m.	n'.	$n'm$.
Helium	1·666	·681	1·135
Hydrogen	1·400	·70	·98
Nitrogen	1·400	·74	1·036
Carbon monoxide	1·400	·74	1·036
Air	1·400	·76	1·064
Oxygen	1·400	·80	1·12
Nitrous oxide	1·333	·93	1·24
Carbon dioxide	1·333	·94	1·25

If the index of V in the writer's equation be made $n'm$, the equation becomes

$$P(V-b)=RTe^{-\frac{\alpha}{T^{\frac{n'(m-1)}{m}}V^{n'm}e^{\frac{m-1}{m}f(T)}}}.$$

The values of RT_c/P_cV_c as given by the figures of the above table vary from 2·6 to 3·8, which gives a range sufficiently wide to account for most of the variations observed. For CO_2 the corresponding equation to (18) becomes

$$\left(\frac{dP}{dT}\right)_V=\frac{P}{T}\{7\cdot76+7\cdot2\lambda T\},$$

which requires a negative value of λ of the order ·00027 to bring it into line with the experimental value of 6·5. The first form of the equation with $M=1$ is, however, preferable on account of its simplicity.

No attempt has been made in the foregoing to enter into a close examination of the numerical values of the various constants for steam. This is reserved for later treatment when more experimental data are available, but, with reference to the question raised earlier as to the determination of the absolute value of λ, it is intended to adopt the value for m as 4/3 in place of 1·3, in conformity with the Kinetic Theory. No doubt 1·3 is a close enough average value for normal steam-engine pressure and temperature ranges, but it cannot hold continuously for all states, unsupported by a hyperbolic

factor. The problem of obtaining the corresponding specific volume to be used in place of that derived from Callendar's formula is one at which, unfortunately, the solution can only be arrived by a somewhat cumbersome process of approximation and trial and error. It would appear, therefore, preferable in the first place to use Callendar's equation for V, and so derive relative values for λ. The relative variation of this is then made apparent and, if it becomes pronounced, the process of approximation referred to must be carried out in order to get the absolute values. Thus, equation (9) may now be written

$$P(V-b)=RTe^{-\frac{\alpha}{T^3Ve^{3\lambda T}}}.$$

This may be solved graphically for V, the most probable value of α being determined from Callendar's tabulated specific volumes at normal temperature and pressure ranges, while the value of λ will have to be tentatively assumed, a guide to its value being derived from the already obtained relative value. If, then, the new value of λ experimentally obtained in conjunction with this tentative specific volume does not agree with the assumed value, further readjustment on the same lines will have to be made until approximate agreement is reached. Fortunately it does not appear that much of this labour will be necessary at the temperatures and pressures which it will be possible to realize, and, in general, the relative values will give sufficiently reliable indication of the specific heat changes which are taking place.

It is interesting to note, in conclusion, that the derived equation of state,

$$P(V-b)=RTe^{-\frac{\alpha}{T^3Ve^{3f(T)}}},$$

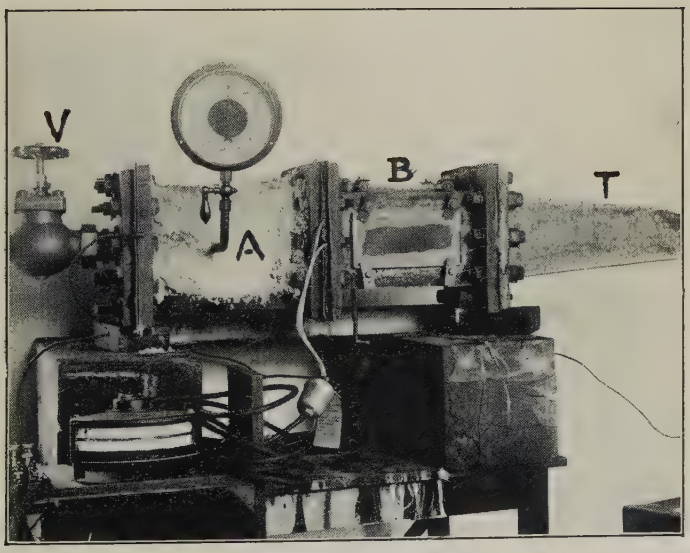
may be written in the following approximate form, assuming $f(T)$ to be a term of small coefficients, say λT,

$$V=\frac{RT}{P}-\frac{\alpha R}{PT^2V}(1-3\lambda T)+b,$$

which is similar to Callendar's equation with the term

$$\frac{\alpha R}{PT^2V}(1-3\lambda T) \text{ in place of } \cdot 0263\left(\frac{373}{T}\right)^{10/3}.$$

Dimensionally, of course, the equations are the same, but the equivalent index of T in the new equation becomes 3 instead of 10/3, and further possible variations are allowed for by the variations which occur in the values of λ.


V
A
B
T

CXXXV. *The Frequencies of Vibration of Flat Circular Plates fixed at the Circumference.* *By* H. Carrington, *B.Sc.(Vict.), M.Sc.(Tech.), A.M.I.M.E.**

THE frequencies of the transverse symmetrical vibrations of a fixed circular plate are given by

$$n = \frac{tz^2}{4\pi a^2}\sqrt{\frac{Eg}{3\rho(1-\sigma^2)}},$$

where n = number of vibrations per sec., t = thickness and a = radius of plate, E = Young's Mod., σ = Poisson's Ratio, ρ = weight per unit volume, g gravitational constant, and the values of z are given by the roots of the equation

$$\frac{J_{n+1}(z)}{J_n(z)} + \frac{I_{n+1}(z)}{I_n(z)}\dagger = 0. \quad . \quad . \quad . \quad . \quad (1)$$

This equation can be solved by interpolation from tables of Bessel functions such as those given by Watson ‡. There are an infinite number of roots for each value of n which represents the number of nodal diameters. For instance, when $n = 0$—*i. e.* no nodal diameters—the roots in order of magnitude correspond with 0, 1, 2, ... nodal circles, and similarly when $n = 1, 2, 3, \ldots$. In cases, however, where $n > 1$, formula (1) cannot be directly applied, and recourse has to be had to reduction formulæ, as there are no tables of $I_n(z)$ where $n > 1$, nor none for $J_n(z)$, with sufficiently small differences in the argument z to render interpolation practicable. These formulæ are

$$\frac{2n}{z}J_n(z) = J_{n-1}(z) + J_{n+1}(z) \text{ and } \frac{2n}{z}I_n(z) = I_{n-1}(z) - I_{n+1}(z)\,\S.$$

Hence, when $n = 1$, formula (1) becomes

$$\frac{J_0(z)}{J_1(z)} - \frac{I_0(z)}{I_1(z)} = 0; \quad . \quad . \quad . \quad . \quad . \quad (2)$$

when $n = 2$,

$$\frac{4}{z} - \frac{J_0(z)}{J_1(z)} - \frac{I_0(z)}{I_1(z)} = 0\,; \quad . \quad . \quad . \quad . \quad (3)$$

* Communicated by the Author.
† Lord Rayleigh, 'The Theory of Sound' (Art. 221 *a*).
‡ Watson, 'The Theory of Bessel Functions' (Chap. xx.).
§ *Ibid.* (Art. 2·12).

and when $n = 3$,

$$\frac{\frac{2}{z}J_1(z) - J_0(z)}{\left(\frac{8}{z^2} - 1\right)J_1(z) - \frac{4}{z}J_0(z)} + \frac{\frac{2}{z}I_1(z) - I_0(z)}{\left(\frac{8}{z^2} + 1\right)I_1(z) - \frac{4}{z}I_0(z)} = 0. \quad (4)$$

As many roots of equations (1) to (4) as can be calculated within the limits of the tables, *i. e.* all the roots < 16, are tabulated below. Five figures were used throughout the calculations.

TABLE I.

S.	$n = 0$.	$n = 1$.	$n = 2$.	$n = 3$.
0.....	3·1961	4·6110	5·9056	7·1433
1..,...	6·3064	7·7993	9·1967	10·537
2.....	9·4395	10·958	12·402	13·795
3.....	12·577	14·108	15 579	—
4.....	15·716	—	—	—

The evaluation of the roots even with the assistance of tables is troublesome, and becomes increasingly so as n increases. Moreover, the tables cease to be of assistance when the magnitude of the roots > 16 and series for the Bessel functions have to be used. The accurate determination of the lower roots beyond the limits of the tables has to be effected by the ascending series for the functions. The higher roots and approximate values for the lower ones can, however, more easily be obtained from the semi-convergent descending series for the same functions. These are

$$J_n(z) = \left(\frac{2}{\pi z}\right)\{P\cos\theta - Q\sin\theta\},\ I_n(z) = \frac{e^z}{\sqrt{2\pi z}}\{P_1 - Q_1\},$$

where

$$\theta = \left\{z - \frac{\pi}{4}(2n+1)\right\},$$

$$P = 1 - \frac{(4n^2-1^2)(4n^2-3^2)}{\underline{|2}(8z)^2} + \ldots,$$

$$Q = \frac{4n^2-1^2}{\underline{|1}(8z)} - \frac{(4n^2-1^2)(4n^2-3^2)(4n^2-5^2)}{\underline{|3}(8z)^3} + * \ldots,$$

* *Ibid.* (Art. 7·1 and 7·3).

and P_1 and $Q_1 = P$ and Q respectively, with the signs between the terms all positive. It follows from known properties of these series that when z is large compared with n, $P = P_1 = 1$ and $Q = Q_1 = 0$ approximately. Hence equation (1) becomes

$$\tan\theta = -1$$

$$\text{or} \quad z - \frac{\pi}{4}(2n+1) = \frac{3}{4}\pi, \quad \frac{7}{4}\pi \ldots = \frac{3}{4}\pi + s\pi;$$

$$i.e. \qquad z = \frac{\pi}{2}(2s+n+2), \quad \ldots\ldots \quad (5)$$

where s is the number of nodal circles.

For moderately large values of z a more accurate approximation than (5) can be used. Let P', Q', P_1' and Q_1' represent P, Q, P_1, and Q_1 respectively when n is replaced by $n+1$.

Then

$$\frac{J_{n+1}(z)}{J_n(z)} = \frac{P'\sin\theta + Q'\cos\theta}{P\cos\theta - Q\sin\theta} \quad \text{and} \quad \frac{I_{n+1}(z)}{I_n(z)} = \frac{P_1' - Q_1'}{P_1 - Q_1},$$

and equation (1) becomes

$$\frac{P'\sin\theta + Q'\cos\theta}{P\cos\theta - Q\sin\theta} + \frac{P_1' - Q_1'}{P_1 - Q_1} = 0$$

$$\text{or} \quad \tan\theta = \frac{P(P_1' - Q_1') + Q'(P_1 - Q_1)}{Q(P_1' - Q_1') - P'(P_1 - Q_1)}.$$

On inserting the values for the series and simplifying as far as z^4, this becomes

$$\tan\theta = -\frac{1 - B/(8z)^2 + C/(8z)^3 - D/(8z)^4}{1 - A/(8z) + B/(8z)^2 - D/(8z)^4}, \quad \ldots \quad (6)$$

where

$$A = 2(4n^2-1),$$

$$B = (4n^2-1)(4n^2-9),$$

$$C = \frac{2}{3}(4n^2-1)(4n^2-9)(4n^2-13),$$

$$D = \frac{1}{6}(4n^2-1)^2(4n^2-9)(4n^2-25).$$

As an indication of the accuracy of these equations, when z is not large, equation (5) gives the root for $n = 0$ and $s = 4$ as 15·70796, whereas from the tables it is 15·71638. Also

for $n = 3$ and $s = 0$, equation (6) gives 7·143558 compared with 7·143261 from the table, all the calculations being to seven figures

A table containing five values of z^4, *i. e.* the first three for $n = 0$ and the first for $n = 1$ and $n = 2$, has been constructed to four figures by Prescott *, with the exception of which the calculation of the periods for fixed circular plates has received little consideration. The periods are mentioned by Lord Rayleigh as being of some practical importance, because of the use of such plates in the telephone. The case of the free circular plate has been considered by Kirchhoff †, who constructed a table analogous to the one given in this paper, and also devised formulæ similar to (5) and (6).

CXXXVI. *Potential Difference and Equilibrium across a Semipermeable Collodion Membrane in the case of Sodium Chloride and Congo Red.* *By* Ryotaro Azuma *and* Naoto Kameyama ‡.

1. Introduction.

When an electrolyte KA is in distribution equilibrium between two solutions separated by a membrane which is permeable to the electrolyte and the solvent, the activities of the electrolyte must be equal; that is,

$$\frac{(a_{KA})_1}{(a_{KA})_2} = \frac{(a_K)_1 \cdot (a_A)_1}{(a_K)_2 \cdot (a_A)_2} = 1.$$

The activity of a substance in a solution is generally more or less affected by the presence of other substances. Therefore, if there be any substance in one of the compartments which cannot pass through the membrane, or which does so with a velocity that is practically negligible in comparison with that of the distributing electrolyte, the concentrations of the electrolyte on the two sides of the membrane will not generally be equal in the equilibrium state although the activities must be equal. Especially the presence of another electrolyte KR with one ion K in common with the distributing

* Prescott, 'Applied Elasticity' (Art. 336).

† *Ibid.* (Art. 335); and Lord Rayleigh, 'The Theory of Sound' (Art. 219).

‡ Communicated by Prof. F. G. Donnan, F.R.S.

electrolyte and the other ion R unable to pass through the membrane will cause a marked unequal distribution of KA, since a_K, and hence a_{KA}, will be increased.

The potential difference between two solutions due to this unequal distribution will be given by the equation

$$E_2 - E_1 = \frac{RT}{F} \log \frac{(a_K)_1}{(a_K)_2} = \frac{RT}{F} \log \frac{(a_A)_2}{(a_A)_1}.$$

The above theory was developed thermodynamically by Donnan in 1911, and experimental results in support of it have been afforded by him and by others.

The present paper deals with the distribution of sodium chloride across a collodion membrane, the solution on one side also containing Congo Red.

2. Experimental.

Purification of Congo Red.

The Congo Red (as obtained from Messrs. Hopkins & Williams) was found to contain about 30 per cent. of sodium chloride. From 100 c.c. of solution saturated at 16°–17°, 5·1 grams of dry residue were obtained, of which 3·5 grams were Congo Red and 1·6 grams sodium chloride. For purification, Harrison's method * was tried and found satisfactory. 20 grams of the commercial dye were put into 250 c.c. saturated ammonium carbonate solution, well shaken, and kept overnight at room temperature, after which the mixture was centrifuged. This treatment was repeated several times until the supernatant solution gave no reaction for chloride. The paste of Congo Red was then evaporated to dryness in an oven at a temperature of 105° for over 24 hours. In a control experiment, a few hours were found sufficient in the same oven to evaporate and volatilize 100 c.c. of saturated ammonium carbonate solution, until both ammonia reaction with Nessler's reagent and carbonate reaction with baryta were negative. The dried material thus obtained was finely powdered in an agate mortar, put into a glass tube connected with a Töpler pump, and warmed slowly under reduced pressure until every sign of gas evolution ceased.

The purified Congo Red was a little darker in colour than the original material. The brownish colour of the pure Congo Red solution was converted into a bright red by a

* Journ. Soc. Dyers & Colourists, 1911, p. 44.

minute quantity of sodium chloride. In order to ascertain the precipitating action of sodium chloride on a Congo Red solution, 2 c c. portions of salt solutions varying in concentration from 0·05 to 6 molar were added to 2 c.c. portions of a 0·0086 molar Congo Red solution, and the mixed solutions kept overnight. In this way it was found that an 0·0043 molar Congo Red solution could be made 0·05 molar with respect to common salt without any precipitation occurring.

Preparation of the Collodion Membrane.

The collodion solution (12–14 per cent.) supplied by the Necol Company was used. It was put into a 250 c.c. test-tube and poured out under slow uniform rotation. The thin membrane thus made was found to permit the passage of Congo Red easily, especially if the solution was fairly concentrated. Therefore a thick and fairly solid cast was made by repeating the procedure two or three times. When the evaporation of ether was complete after drying for 10 to 15 minutes, the tube with the collodion cast was put into water for about 10 minutes until the collodion bag became detached. This thick type of collodion membrane was found to be impermeable to Congo Red for the duration of the experiments, which lasted usually seven to ten days. The permeability of the membrane to sodium chloride was tested before each experiment by putting a sodium chloride solution of appropriate concentration into the bag and placing the latter in water. The equalization of the salt concentrations on both sides of the membrane was found complete within 24 to 48 hours.

Method of Analysis.

In order to estimate sodium chloride in a Congo Red solution, nitric acid was added until the red colour disappeared, and the blue precipitate washed on a filter with water slightly acidified with nitric acid. The clear filtrate thus obtained was titrated by Volhard's method, using 0·1N $AgNO_3$ and 0·1N KCNS. This method of determining the amount of sodium chloride in a Congo Red solution proved to be an accurate one.

With regard to the analysis of the equilibrium solutions, it must be recollected that a very considerable amount of the Congo Red is absorbed by the membrane. This amount,

as Bayliss pointed out, depends on the concentration of the other electrolytes present, and was found in the present experiments to vary from 10 to 60 per cent. of the amount initially present, according to the different concentrations of Congo Red and sodium chloride. In order, therefore, to determine the amount present in the final equilibrium solution, the total solid residue was weighed after evaporation of the solution to complete dryness, the sodium chloride in it ascertained, and the difference taken as Congo Red.

Apparatus and Measurement of Potential Difference.

The diffusion vessel was a glass cylinder of 350 c.c. capacity, inside which the collodion bag was hung. The cylinder had a cork stopper with two short glass tubes, one of which communicated with the space outside the bag, whilst the other passed through a rubber stopper tightly fitted to the bag. Usually these two tubes were connected with soda-lime tubes, so that the two solutions were exposed only to air free from carbon dioxide and at atmospheric pressure. The solution inside the bag was invariably the mixed solution of Congo Red and sodium chloride, whilst the outside solution usually contained only sodium chloride, although in a few cases the mixed solution was also placed here. With this arrangement equilibrium was attained within four or five days, but the experiment was continued generally for a week, with occasional gentle shaking of the apparatus. When the potential difference was to be measured, the soda-lime tubes were removed and gelatine-salt bridges inserted in place of them, in order to make electrical connexion of the two solutions with outside N. KCl solutions, into which the tubes of N. KCl calomel electrodes dipped. These electrical connexions were the chief difficulty in the measurements, as Congo Red is easily precipitated by salt solutions above a certain concentration. The gelatine-salt bridges were used in order to avoid direct contact of the N. KCl solution with the equilibrium solutions. The bridges consisted of two thin glass U-tubes filled with 10 per cent. gelatine jelly in 0·05 to 0·1 N NaCl solution, the gelatine used being a purified and practically ash-free sample. The precision of the electrical measurements was $\pm 0{\cdot}02$ millivolt.

Two kinds of cells were measured, the first one with the membrane and the solutions in equilibrium, the second one without membrane and Congo Red, but otherwise the same.

They may be represented in the following manner, where N.E.=normal calomel electrode, B=gelatine-salt bridge, ‖=the membrane, C.R.=Congo Red, c=concentration.

$$\underset{e_1}{\text{N.E.}-\text{N.KCl}-}\underset{e_2}{\text{B}-}(\text{C.R.}+\text{NaCl}\,c_1)\,\|\,\underset{E_m}{\text{NaCl}(c_2)}\underset{e_3}{-\text{B}-}\underset{e_4}{\text{N.KCl}-\text{N.E.}}, \quad . \quad . \quad (1)$$

$$\underset{e_1}{\text{N.E.}-\text{N.KCl}-}\underset{e_2'}{\text{B}-}\underset{E_d}{\text{NaCl}(c_1)-\text{NaCl}(c_2)}\underset{e_3}{-\text{B}-}\underset{e_4}{\text{N.KCl}-\text{N.E.}} \quad . \quad . \quad (2)$$

The various junction potentials are indicated, E_m being the potential across the collodion membrane, and E_d the direct diffusion potential between the two solutions of sodium chloride. It is obvious that e_1 and e_4 are equal in magnitude and opposite in sign. If E denote the E.M.F. of cell 1, and E′ that of cell 2,

$$E_m = E_d + (E - E') + (e_2' - e_2).$$

E_d can be calculated from the analytical results and other known data. If it be assumed that $e_2 = e_2'$, E_m can be determined from the measured values of E and E′ and the calculated values of E_d. In order to obtain reproducible values for E_d and to avoid mixing, a small glass tube with a well-fitted ground-in stopper was used in cell 2 to connect the two solutions of sodium chloride. Before and after every experiment it was tested whether any potential difference existed across the collodion membrane when separating two solutions of sodium chloride of the same concentration. None was found. There existed, therefore, no disturbing internal E.M.F. inside the membrane, even though it was stained with adsorbed Congo Red on one side.

3. Results of the Distribution Experiments.

The results are shown in columns B to E in Table 1. The inequality in the equilibrium distribution of NaCl is shown by the divergence of the ratio c_1/c_2 from unity. It will be seen that the more concentrated the Congo Red, the more marked is the unequal distribution. In the present case the equilibrium equation is

$$(a_{\text{Na}})_1 \cdot (a_{\text{Cl}})_1 = (a_{\text{Na}})_2 \cdot (a_{\text{Cl}})_2.$$

Writing $a_{Na}=f_{Na}\cdot m_{Na}$, where f_{Na} and m_{Na} denote the activity coefficient and stoichiometrical molarity respectively of sodium ion, and corresponding equations for chlorine ion, the equilibrium equation takes the form

$$(f_{Na}\cdot f_{Cl})_1\cdot(m_{Na}\cdot m_{Cl})_1=(f_{Na}\cdot f_{Cl})_2\cdot(m_{Na}\cdot m_{Cl})_2.$$

If, following G. N. Lewis, we write

$$f_1^2=(f_{Na}\cdot f_{Cl})_1,$$
$$f_2^2=(f_{Na}\cdot f_{Cl})_2,$$

where f_1 and f_2 denote the "mean activity coefficients" of sodium chloride in solutions 1 and 2 respectively, we have

$$f_1^2(m_{Na}\cdot m_{Cl})_1=f_2^2(m_{Na}\cdot m_{Cl})_2.$$

Introducing, further, the "mean molarities"

$$m_1^2=(m_{Na}\cdot m_{Cl})_1,$$
$$m_2^2=(m_{Na}\cdot m_{Cl})_2,$$

the equilibrium may be written

$$f_1m_1=f_2m_2,$$

or simply $a_1=a_2$, where a_1 and a_2 denote the "mean activities."

For equilibriums we must have therefore

$$a_1/a_2=f_1m_1/f_2m_2=1.$$

The values of m_{Na} and m_{Cl} for the pure solutions of NaCl are assumed to be equal to the molar concentrations as determined by analysis, since the solutions are all dilute. The same assumption may be made with regard to m_{Cl} in the mixed solution of sodium chloride and Congo Red. For the calculation of m_{Na} and of f in the mixed solutions, the following two assumptions have been made:—

(1) It is assumed that in the range of concentrations examined, Congo Red behaves as a uni-univalent strong electrolyte; *i. e.*, that it ionizes according to the equation

$$\overset{v}{Na_2R}=Na^+ + (NaR)^-.$$

(2) It is assumed that in the range of concentrations here investigated the "ionic strength principle" of G. N. Lewis holds good; *i. e.*, that the mean activity coefficient of sodium chloride, whether in a pure aqueous solution or in a mixed

solution with Congo Red, is a function solely of the ionic strength (μ) of the solution.

As regards the calculation of m_{Na} in the mixed solution, the first assumption amounts only to assuming the presence ot one sodium ion per chemical (Avogadrian) molecule of Congo Red added to the solution. It would therefore be in harmony with the assumption that in the range of concentrations investigated there is produced in the solution, per Avogadrian molecule dissolved, one sodium ion and one large micellar anion, for which assumption there is some support to be found in the measurements of the osmotic pressures of Congo Red solutions. But as regards the calculation of μ, the assumption made amounts to assuming the existence in the solution, per Avogadrian molecule of Congo Red, also of one univalent anion (NaR). From the point of view, however, of the ionic strength principle or of the theory of Debye and Hückel, it does not follow that a relatively small concentration of a large highly-charged anionic micelle would be equivalent in effect to a relatively high concentration of a simple univalent anion. We have also to take into account the recent views of Einer Hammarsten on the effect of the field of a large anion on the effective (osmotic) activity of a small cation. It must be admitted, therefore, that in the present state of knowledge the first assumption made above can be regarded only as a tentative one.

There is considerable support for the second assumption when we are dealing with sufficiently dilute solutions of simple electrolytes, though the theory of Debye and Hückel would lead to the conclusion that the large anions or anionic micelles which exist or may exist in a solution of Congo Red would increase the activity coefficient of chlorine ion more greatly than according to the ionic strength principle of Lewis.

From the first assumption we have

$$m_{Na} = c_{NaCl} + c_{Na_2R}$$

and

$$\frac{(m_{Na} \cdot m_{Cl})_1}{m_{Na} \cdot m_{Cl})_2} = \frac{c_1 + c_{Na_2R}}{c_2 + c_{Na_2R}} \cdot \frac{c_1}{c_2}.$$

The values of this ratio are given in column F of the Table *.

* All concentrations given in the table are expressed as millimols per litre.

TABLE I.

A.	B.	C.	D.		E.	F.	G.	H.	I.	J.	K.	L.
	Experimental Data.					Congo Red uni-valent.				Congo Red uni-bivalent.		
Exp. No.	Solution 1.		Solution 2.		c_1. c_2	$\frac{(m_{Na} \cdot m_{Cl})_1}{(m_{Na} \cdot m_{Cl})_2}$.	f_1.	f_2.	$\frac{a_1}{a_2}$.	$\frac{(m_{Na} \cdot m_{Cl})_1}{(m_{Na} \cdot m_{Cl})_2}$	$\frac{a_1}{a_2}$.	$\frac{100\,C_{Na_2R}}{C_{NaCl}\text{ in Sol. 1}}$.
	Congo Red. c_{Na_2R}.	NaCl. c_1.	NaCl. c_2.									
1 ...	2·0	50·2	51·0		0·984	1·007	0·839	0·8405	1·002	1·046	1·016	4·0
2 ...	3·1	28·4	29·6		0·959	1·021	0·868	0 871	1·007	1·121	1·043	10·9
3 ...	4·3	32·4	34·0		0·953	1·028	0·860	0·8635	1 010	1·147	1·051	13·3
4 ...	3 9	28·0	29·9		0·937	0·999	0·867	0·871	0·995	1·121	1·040	13·9
5 ...	5·5	19 3	21·3		0·906	1·055	0·882	0·889	1·019	1·289	1·099	28·5
6 ...	4·8	14·7	16·3		0·902	1·078	0·893	0·9015	1·028	1·345	1·121	32·7
7 ...	6·0	10·5	12·2		0·861	1·163	0·901	0·9135	1·064	1·587	1·204	57·2
8 ..	5·9	12·5	14·9		0·839	1·036	0·896	0·905	1·008	1·368	1·122	47·2
9 ...	5·3	15·1	17·0		0·888	1·066	0·891	0·8995	1·023	1·343	1·120	35·1
10 ...	6·0	6·4	8·0		0·800	1·240	0·913	0·930	1·093	1·840	1·288	93·8
			C. R.	NaCl.								
11 ...	1·29	56 5	0·52	57·4	0·984	0·932	0 8325	0·832	0·992	0·995	0·996	2·3
12 ...	6·66	10·8	0·46	13·0	0·831	1·077	0·898	0·9095	1·025	1·440	1·150	61·7
13 ...	6·30	31·9	0·47	33·8	0·944	1·052	0·859	0·8635	1·019	1·209	1·073	19·7

In order to obtain the required values of f (mean activity coefficient of sodium chloride), a curve of f as a function of $\mu^{\frac{1}{2}}$ was drawn from the known data * for pure aqueous NaCl solutions at 25°, and the values interpolated from the curve at the required values of the ionic strength μ. For the mixed solutions,

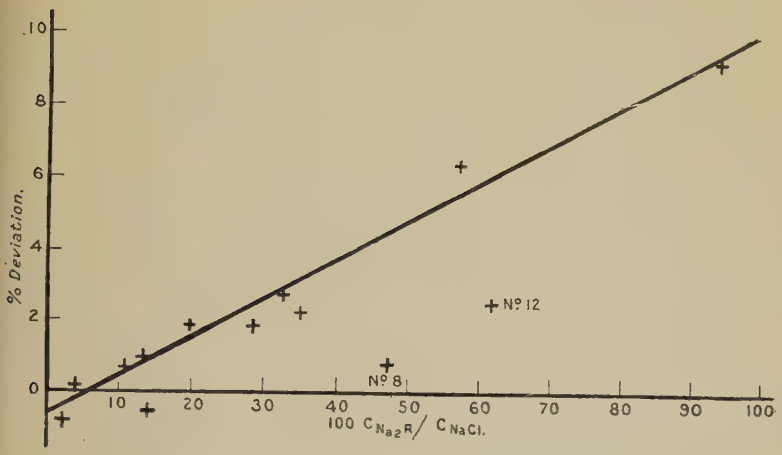
$$\mu = \tfrac{1}{2}(m_{Na} + m_{Cl} + m_{NaR}) = c_{NaCl} + c_{Na_2R},$$

and for the pure solutions of sodium chloride, $\mu = c_{NaCl}$. Columns E, G, and H of the table give the calculated values of f_1, f_2, and a_1/a_2 respectively. According to the theory, the ratio a_1/a_2 should be unity. Two remarks may be made here. The activity-coefficient curve for NaCl drawn from the data of Lewis refers to molarities per kilogram of water, whilst we have employed in the calculation of our experimental results molarities per litre. Owing to the dilution of the solutions, however, this difference of procedure introduces only a very small error. The data given by Lewis refer to 25°, whilst our experiments were made at room temperature (17–19°). Since we only assume in the calculation of a_1/a_2 that in the temperature range (18–25°) the temperature coefficient of f is the same in a pure solution as in a mixed solution with Congo Red, no sensible error can arise from this source.

For the sake of comparison, columns J and K of the table show values calculated on the assumption that Congo Red behaves as a strong uni-bivalent electrolyte, ionizing according to the equation $Na_2R = 2Na^+ + R^{--}$. In the last column of the table are given values of $100c_{Na_2R}/c_{NaCl}$ in the inside (mixed) solution, in order to exhibit more clearly the relation between this quantity and the deviation of a_1/a_2 from unity. It will be obvious from an examination of the table that the ratio a_1/a_2 deviates widely from unity when we assume that Congo Red acts as a strong uni-bivalent electrolyte. The results given in column I show that, with the assumptions made in this paper, the activity ratio of sodium chloride is not quite equal to unity, as the theory requires. The deviations from unity are, however, less than 3 per cent. in eleven out of thirteen experiments. There seems to be a distinct tendency for this deviation to increase with increasing values of the ratio c_{Na_2R}/c_{NaCl}, as shown in fig. 1.

* Lewis and Randall, 'Thermodynamics and Free Energy of Substances,' p. 362.

Fig. 1.



4. Results of the E.M.F. Measurements.

These results are shown in Table II. All values are expressed in millivolts. The sign of the E.M.F. is taken positive when "positive" electricity tends to pass from solution 1 (inside the collodion bag) to the outside solution 2.

Table II.

Exp. No.	Experimental Data. E.	E′.	E-E′′.	Calculated Values. E_m.	E_d.	E_m-E_d.	f_1'.
1.....	0·07	−0·02	0·09	0·445	0·077	0·368	0·8415
2.....	0·07	−0·01	0·08	1·127	0·204	0·923	0·8735
3.....	−0·19	−0·15	−0·04	1·317	0·237	1·080	0·8665
4.....	0·075	0·065	0·01	1·762	0·325	1·437	0·8745
5.....	−0·17	−0·39	0·22	2·686	0·490	2·196	0·894
6.....	0·13	0·03	0·10	2·825	0·518	2·307	0·906
7.....	0·83	0·54	0·29	4·113	0·757	3·356	0·9195
8.....	−0·45	−0·41	0·04	4·656	0·878	3·778	0·913
9.....	−0·30	0·11	−0·41	3·207	0·592	2·615	0·905
10.....	−2·56	0·16	−2·72	6·060	1·131	4·929	0·938
11.....	7·60	7·48	0·12	0·381	0·076	0·305	0·833
12.....	2·422	1·95	0·47	4·968	0·931	4·037	0·911
13.....	0·66	0·80	−0·14	1·624	0·283	1·341	0·864

E_m has been calculated from the equation

$$E_m = 0{\cdot}05777 \log \frac{(m_{Cl} \cdot f_{Cl})_2}{(m_{Cl} \cdot f_{Cl})_1} = 0{\cdot}05777 \log \frac{f_2 c_2}{f_1 c_1},$$

where, as the solutions are dilute, it is assumed that

$$f = f_{NaCl} = \sqrt{f_{Cl} \cdot f_{Cl}} = f_{Cl}.$$

Thus the values of E_m have been calculated from the figures given in columns E, G, and H of Table I.

The exact equation for the potential difference (E_d) at the junction of two solutions of sodium chloride of molarities m_1 and m_2 is *

$$E_d = \frac{RT}{F}\left[\log \frac{(a_{Cl})_2}{(a_{Cl})_1} - \int_{m_1}^{m_2} t\,d\,(\log a_{NaCl})\right],$$

where t = transport number of sodium ion. This transport number is practically constant in the range of concentration here in question and equal to 0·395. Assuming also that $f_{Na} = f_{Cl}$, we get

$$E_d = (1-2t)\frac{RT}{F}\log\frac{(a_{Cl})_2}{(a_{Cl})_1} = (1-2t)\frac{RT}{F}\log\frac{(m_{Cl} \cdot f_{Cl})_2}{(m_{Cl} \cdot f_{Cl})_1}$$

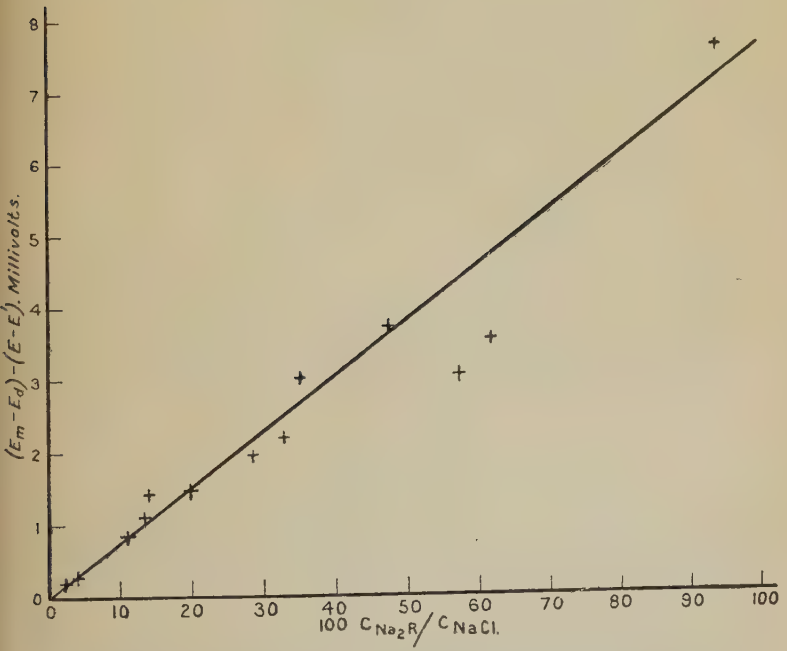
$$= 0{\cdot}210 \times 0{\cdot}05777 \log_{10}\frac{f_2 c_2}{f_1 c_1}.$$

It is necessary to note that, in the measurement of E′ and the calculation of E_d, solution 1 is not the same as the solution 1 used in the measurement of E and the calculation of E_m, since the former solution contained the same concentration of sodium chloride but no Congo Red. Its ionic strength is therefore less. The corresponding values of f_1' are given in the last column of Table II. An examination of Table II. reveals the fact that E − E′ is very small in comparison with $E_m - E_d$, whereas, if the assumption $e_2 = e_2'$ be justified (see p. 1268), $E_m - E_d$ must be equal to E − E′. It would follow from this result that, if the above assumption be justified, the actual potential difference across the collodion membrane must be very much smaller than the calculated value and of the order of magnitude of E_d, *i. e.* of the nature of a diffusion potential. The other alternative is that $e_2' - e$ is not small, and that it balances a considerable portion

* *Cf.* Lewis, *loc. cit.* p. 338.

of the true membrane potential. In the case of the e_2-junction there was present Congo Red in the aqueous solution, whereas this substance was absent in the case of the e_2'-junction. The two ions of sodium chloride can readily pass through the gelatine-water interface, whereas, in the case of the 10 per cent. gelatine-jelly used, the anion of Congo Red does not pass through this interface, or only with extreme slowness. It is therefore possible that a "membrane potential" was set up at the junction, gelatine-salt jelly—aqueous solution of sodium chloride and Congo Red.

Fig. 2.



As shown in fig. 2, the difference between $E_m - E_a$ and $E - E'$, which is equal to $e_2' - e$, increases markedly as the value of c_{Na_2R}/c_{NaCl} in the mixed solution increases.

Summary.

1. The potential differences and ionic equilibria across a semi-permeable collodion membrane in the case of aqueous solutions of sodium chloride and of sodium chloride plus Congo Red have been measured.

2. If Congo Red in the range of concentrations measured be assumed to ionize as a uni-univalent electrolyte, and if the ionic strength principle of G. N. Lewis be assumed to hold good for the mixtures of Congo Red and sodium chloride used, the experimental results are in general agreement with the thermodynamical requirement of the equality of the activities of sodium chloride on either side of the membrane.

3. Owing to the difficulty of eliminating liquid-liquid potentials in solutions containing Congo Red, it has not been possible to prove that the potential difference across the membrane is in agreement with the thermodynamical requirement for a system in equilibrium.

The authors desire to express their best thanks for advice and assistance to Professor F. G. Donnan, at whose suggestion this investigation was undertaken.

The William Ramsay Laboratories of
Physical and Organic Chemistry,
University College, London.
March 1925.

CXXXVII. *The Spectrum of Rubidium at Low Voltages.* *By* F. H. Newman, *D.Sc., A.R.C.S., Professor of Physics in the University College of the South-West of England, Exeter* *.

[Plate XXXVII.]

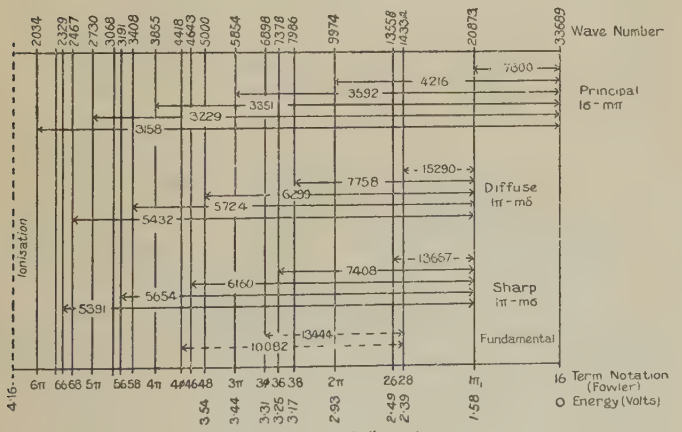
1. Introduction.

THE author has described previously † an investigation of the effects of electron collisions with sodium and potassium atoms whereby a line-by-line radiation emission, corresponding to interorbital transitions involving less energy than the ionizing potential, resulted as the velocity of the impacting electrons was progressively increased. Absorption and fluorescence phenomena prove that the valency electron within an atom of an alkali metal can be displaced directly from the normal orbit—1σ—to any of the π orbits, but the subordinate series lines are not absorbed unless the alkali vapour is thermally, optically, or electrically stimulated, in which cases we may assume that the electron within the atom is not in the 1σ level but has

* Communicated by the Author.
† Phil. Mag. l. p. 165 (1925), and l. p. 796 (1925).

been displaced to the 1π orbit, from whence, according to Sommerfeld's selection principle, it may be displaced directly to any of the $m\delta$ or $m\sigma$ orbits, giving rise to absorption of the subordinate series lines. It is reasonable to assume that impacting electrons of the requisite energy should, by their collisions with atoms, raise the valency electron to various energy levels permitted by the selection principle, and as a result various lines should be radiated when the displaced electron in the different atoms returns to the normal orbit. In the previous investigations these theoretical considerations were verified experimentally. Electrons emitted from a heated tungsten-wire cathode in a three-electrode discharge tube were accelerated by a potential difference applied between the grid and the cathode, and entering a force-free space between the grid and anode excited radiation within this space.

Fig. 1.



Graphical representation of rubidium atom.

Considering the case of rubidium, fig. 1 shows a graphical representation of the energy levels within the rubidium atom. Supposing the nucleus situated to the right, the vertical lines represent parts of the non-radiating orbits, and emission lines result when the electron within the atom falls from orbits on the left to orbits on the right, the electron having been displaced previously to the left by optical or electrical stimulation. It will be noted that in the absence of strong electric fields, whether external or internal, *i. e.*, in the absence of any Stark effect, not all

possible transitions are allowed by the selection principle, but only those in which the azimuthal quantum number changes by unity, so that as the azimuthal quantum numbers corresponding to the $m\sigma$, $m\pi$, $m\delta$, and $m\phi$ orbits are 1, 2, 3, and 4 respectively, interorbital transitions from the $m\pi$ to the $m\sigma$ or the $m\delta$ levels are possible, but falls from the $m\sigma$ to the $m\delta$ are precluded. In the diagram the vertical lines really represent portions of the elliptic orbits about the nucleus, 1σ being the outermost stable orbit; the $m\pi$ rings are really double, but their separation is too small to be represented. In all cases the horizontal lines extending between orbits show the wave-length of the radiation emitted due to interorbital transitions between the orbits, the dotted lines indicating wave-lengths falling outside the range of sensitiveness of the plate.

The energy level of each orbit has also been expressed in terms of the potential difference through which the bombarding electron must fall to accumulate kinetic energy equivalent to the quantum of radiation emitted from the bombarded atom. If ν is the wave number of the spectral line which is produced by the return of the electron from orbit m_2 to m_1, we have

$$V = \frac{\nu}{8102},$$

where V is the potential difference through which the bombarding electron must fall to acquire the requisite amount of energy. Since the ionization potential corresponds to the removal of an electron from the innermost orbit to infinity, m_2 in this case $= \infty$, and the ionization potential is given by substituting for ν the limit of the series which extends furthest into the ultra-violet. It is convenient to consider the work required to displace the electron from an inner to an outer orbit, and hence to the innermost orbit is ascribed zero energy. The energy indicated against any one orbit represents the value which the valency electron must receive in order that it may be displaced from the 1σ level to that orbit. For example, if rubidium atoms are bombarded with electrons of energy 1·58 volts—the resonance potential—the valency electron should be displaced from the 1σ level to the $1\pi_1$ orbit, and the displaced electron being then in a temporary orbit falls back to the 1σ level, giving up the energy eV, received at impact, as a quantum of radiation $h\nu$ of wave number ν. This radiation consists of the first doublet of the principal series—λ 7948, 7800. It will be observed that theoretically it should be possible

to stimulate λ7948 without λ7800, provided that the impacting energy is equal to or greater than 1·55 volts and less than 1·58 volts. In practice, however, it would be difficult, if not impossible, to insure that the impacting energy lies within this small range, because the initial kinetic energy of the individual electrons on emission from an incandescent filament, which is the usual source of electrons, varies by 0·5–1 0 volt.

Bombardment with electrons of 2·39 volts energy should eject the electron within the atom to the 2δ orbit, from which it returns to the 1σ orbit by way of the $1\pi_1$ level, giving rise to λ 15290, which is too far in the infra-red to be photographed, and λ 7948, 7800. From further consideration, it is evident that the second doublet of the principal series—λ 4202, 4216—should appear next, as the impacting energy is raised to 2·93 volts, since transitions from the 2σ to the $1\pi_1$ orbits give rise to λ 13667—far in the infra-red. As there seems to be no reason to suppose that an electron at collision transfers all of its energy to the atom, electrons of 2·93 volts energy should eject the electron within the atom to the $1\pi_1$, 2δ, or the 2σ orbit, in addition to the 2π orbit, in different atoms. Theoretically the following lines should then appear in this order as the bombarding electrons are still further accelerated: λ 7758, 7619 ; λ 7408, 7280 ; λ 3592, 3587 ; λ 6299, 6206 ; λ 6160, 6071, etc., until the complete arc spectrum is radiated at 4·16 volts, the theoretical ionization potential.

Experimental results have shown, however, that under ordinary conditions it is possible to obtain only the single line spectrum—λ 7948, 7800—and the complete arc spectrum, but, as stated in the previous papers, the failure to observe the line-by-line emission is explained by the space charge effect of the electrons lowering the impacting energy except in the immediate vicinity of the anode. The space charge greatly affects the electric field gradient within a discharge tube. This has been verified experimentally by Compton and Eckart *, and the effect of the space charge is particularly evident in the methods largely employed in studying spectrum excitation, where a grid is mounted close to an incandescent filament and in metallic contact with a concentric hollow cylinder of relatively large diameter. By regulating the gas- or vapour-pressure within the discharge tube relatively few electron-atomic collisions occur over the short accelerating field between the grid and the cathode.

* Phys. Rev. xxv. p. 139 (1925).

The majority of the electrons pass into the force-free space between the grid and the plate, but it is only in the immediate neighbourhood of the anode that they have, at the instant of collision, a velocity corresponding to the impressed field, so that spectroscopic observation must be made on the radiation coming from the vicinity of the anode.

2. Experimental Results.

The form of discharge tube employed was similar to that used in the experiments with sodium vapour. Electrons, emitted from a heated cathode consisting of three tungsten wires arranged in parallel, were accelerated by a potential difference applied between the negative end of the cathode and the grid, and entered a constant potential space between the grid and surrounding cylinder. The whole tube, containing a small quantity of rubidium metal, was enclosed within an electric heater the temperature of which was maintained at 150° C., at which temperature the vapour-pressure of rubidium is less than 0·1 mm. of mercury. The discharge tube was continuously exhausted, so that the residual gas-pressure was kept below 10^{-3} mm. of mercury. Light from the immediate vicinity of the anode was focussed on the slit of a quartz spectrograph, and the spectra emitted at different accelerating voltages applied between the cathode and the grid were photographed on special rapid panchromatic plates. The latter were not sensitive beyond λ 7600, but were sensitized for the red end of the spectrum by means of a dicyanin solution which gave satisfactory results.

It is evident that the potential difference, as measured between the cathode and anode, does not give the true energy of the bombarding electrons, for the latter are emitted from the filament with an initial velocity which varies considerably among the various electrons, and, in addition, there is a contact potential and a fall of potential along the lead-in wires and the filament to be taken into account. A correction for these various errors was applied by measuring the ionization potential, and comparing the result with the theoretical value, 4·16 volts. The necessary correction has been made in all the measurements quoted in the paper.

As the accelerating voltage was increased, radiation at first appeared in the vicinity of the grid and plate and was purple in colour, but as the potential was still further raised, the radiation extended from these electrodes, and at the

ionization potential filled the space between the grid and the plate.

The spectrograms obtained at various excitation voltages are shown in Plate XXXVII. At 1·7 volts the first doublet of the principal series, λ 7948, 7800, appeared, as shown in the first spectrogram, but visually the tube appeared dark, as these lines lie outside the range of the visible spectrum. This value of the excitation potential agrees fairly well with the calculated value, 1·58 volts. No more lines were photographed until the potential had been raised to 3·2 volts, when the second doublet of this series, λ 4216, 4202, was excited. This is shown in the second spectrogram. The next lines to be excited should be λ 7758, 7619 and λ 7408, 7280, and they should be emitted at 3·17 volts and 3·25 volts respectively, but even with exposures extending over many hours

TABLE I.

Rubidium lines excited with different applied potentials.

Series.	Wave-length.	Excitation voltage.	
		Experimental.	Calculated.
$1\sigma-1\pi_1$	λ 7948 7800	1·7 volts	1·58 volts
$1\pi_1-2\delta$	λ 15290 14754	—	2·39
$1\pi_1-2\sigma$	λ 13667 13237		2·49
$1\sigma-2\pi$	λ 4216 4202	3·2	2·93
$1\pi_1-3\delta$	λ 7758 7619	3·6	3·17
$1\pi_1-3\sigma$	λ 7408 7280	3·6	3·25
$2\delta-3\phi$	λ 13444	—	3·31
$1\sigma-3\pi$	λ 3592 3587	3·6	3·44
Complete arc spectrum.		4·2	4·16

they could not be detected below 3·6 volts. At this potential they were very faint on the negative, and do not show at all in the third spectrogram, although the third doublet in the principal series, λ 3592, 3587, is prominent. Theoretically, the latter should be emitted at 3·44 volts. Increasing the voltage to 3·8 volts the subordinate series lines λ 7758,

7619 and λ 7408, 7280 became more intense and are shown in the fourth spectrogram, while the complete arc spectrum, obtained at 4·2 volts, is shown in the fifth spectrogram. The different lines excited when the rubidium atoms were bombarded with electrons subjected to various potential differences are shown in Table I.

These results indicate that the spectral lines of rubidium vapour may be excited when the vapour is subjected to bombardment by electrons possessing less energy than that necessary for ionization, this line-by-line emission resulting as the valency electron within the atom is displaced to, and returns from, the various outer non-radiating orbits.

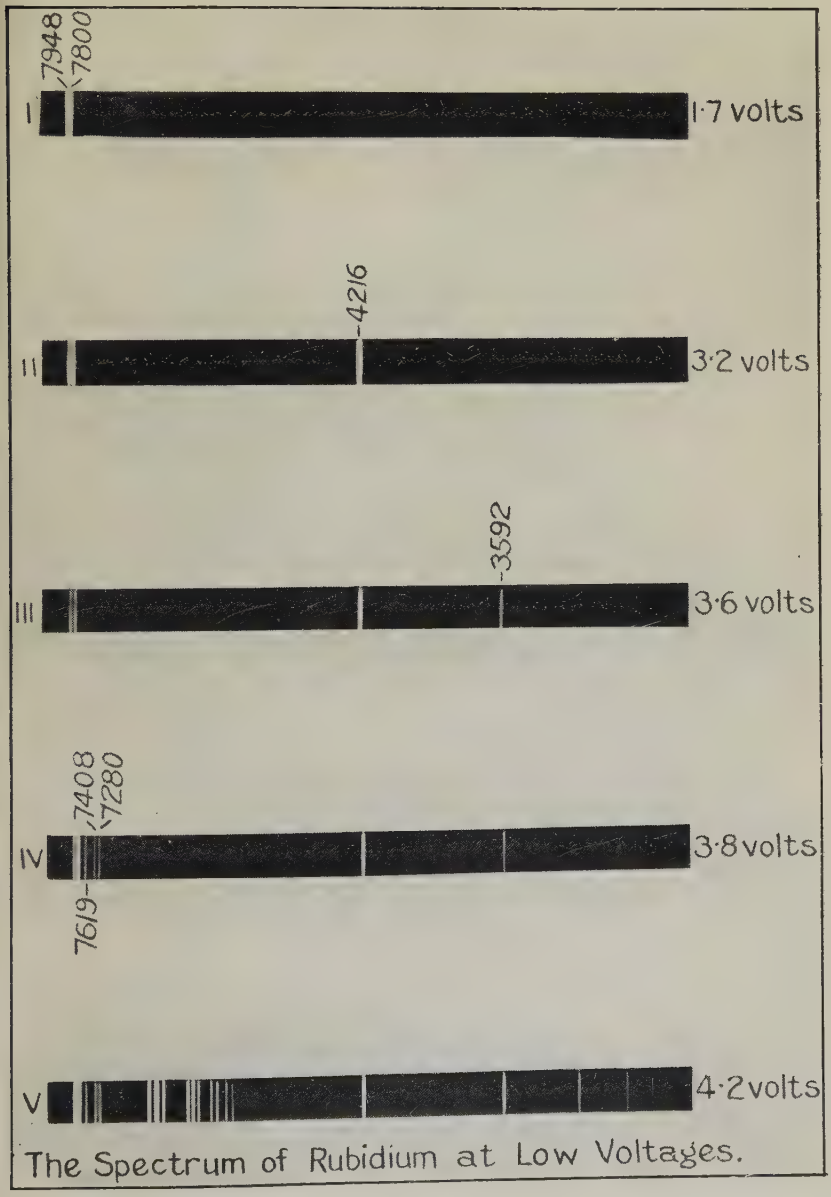
The author wishes to express his thanks for a Government grant from the Royal Society.

CXXXVIII. *A New Optical Phenomenon shown by Biaxal Crystals.* *By* S. R. Savur, *M.A., University College, London**.

ABOUT two years back Prof. Raman and Mr. Tamma described a curious phenomenon which they had discovered in biaxal crystals †. The phenomenon is briefly the following. When a biaxal crystal plate is suitably cut and oriented, it produces a real image of a bright object. This image is continuous (that is, it may be observed anywhere in the prolongation of a certain line), is erect and is of unit magnification. If the object emit white light, the image is coloured. If, however, the object gives out a line spectrum, then there will be an image corresponding to every line, and these will be in the order in which the lines appear in a spectrum.

The above mentioned authors gave an explanation of this highly interesting observation. As will be shown below, their explanation is not quite satisfactory, and appears to be in contradiction with some observations made by me on this phenomenon. In this connexion it is important to note that the phenomenon is produced only when the dimensions of the object are small and when the object is brightly illuminated. This latter fact suggests that the phenomenon may be a secondary effect. It is also produced for a particular

* Communicated by Prof. A. W. Porter, D.Sc., F.R.S., F.Inst.P.
† Phil. Mag. March 1923.



The Spectrum of Rubidium at Low Voltages.

orientation of the crystal plate with respect to the object, which means that it is obtained when the light traverses a particular path inside the crystal. To determine what the direction of this path is with respect to the axes of the crystal, it was obviously necessary to use, what in practice we can obtain, the nearest approach to a ray of light. Accordingly the following experiment was performed.

At a distance of about 150 cm. from a point-o-lite is placed a pin-hole with a colour filter in front of it. The pin-hole thus transmits a very narrow but intense and practically parallel beam of more or less homogeneous light which is refracted by a plate of aragonite crystal whose refracting faces have been cut perpendicular to the acute bisectrix of the angle between the optic axes. By suitable orientation of the plate, the phenomenon, which in this case is a very small and bright disk of light, may be obtained on a screen. To study the phenomenon, however, it was found convenient to use a cathetometer, instead of screen, having a micrometer scale in its eyepiece.

When the plane on which the cathetometer is focussed is changed, it is found that the appearance of the phenomenon is altered. A curious fact observed is that the various appearances depend *only* on the distance between the plane on which the cathetometer is focussed and the pin-hole, which shows that the appearances are independent of the position of the plate between the cathetometer and the pin-hole. This important fact, as will be shown subsequently, is not in accordance with the explanation advanced by Prof. Raman and Mr. Tamma. In what follows, "distance" is measured in the direction of the propagation of light and means the distance of the plane, on which the cathetometer is focussed, from another which contains the image of the pin-hole as seen through the slab, and which is between the pin-hole and the crystal and distant 6 mm. from the former.

The light used had a mean wave-length of approximately 6000 Å.U. The diameter of the pin-hole was 0·16 mm. We will consider a few cases.

(*a*) Distance = 20 cm.

We see a circular spot at the centre of a much less bright disk which has a hazy outline. This spot is the phenomenon that is obtained from a point source, and may be called the Raman-Tamma image of the pin-hole formed by the plate.

Diameter of the spot = 0·34 mm.
„ „ disk = 2 mm. roughly.

The disk and the spot are unpolarized.

As the distance of the focussed plane is slowly diminished, the disk shrinks rapidly, becomes brighter and gets a sharper outline. The spot also gains in brightness but diminishes in diameter more slowly.

(*b*) Distance = 10·4 cm.

The disk has broken up into an outer ring whose outer diameter is 1·7 mm. and a disk of hazy outline whose diameter is approximately 0·6 mm. The spot, which is still at the centre of the disk, is very bright and has a diameter of 0·26 mm. Two very faint outer and concentric rings are also seen. When observed through a nicol a dark radial strip is seen in the outer bright ring, and this strip rotates with the nicol but at twice its rate. The disk and the spot are unpolarized.

(*c*) Distance = 3·0 cm.

The inner disk has broken away from the spot and has become a ring. The outer and inner bright rings are separated by a very thin dark ring. The faint outer rings have also closed in and have become somewhat brighter. When examined through a nicol a dark radial strip is seen cutting the rings. The spot is unpolarized.

As the distance is decreased, the dark ring separating the two bright rings remains unchanged in diameter. The rings diminish in thickness slowly and become brighter. The spot enlarges and a ring breaks away from it. This ring becomes bigger and finally merges into the inner bright ring. The spot, which is less bright now, enlarges again, another ring breaks away from it, and the whole process is repeated two or three times, each new ring being fainter than its predecessor. One is reminded of the way in which the rings in a Fabry and Perot's interferometer behave when the distance between the mirrors is slowly diminished. The difference between the two is that in our present case the central spot persists for a long time.

(*d*) Distance is nil.

What is seen is practically a single bright ring. The spot has vanished.

Outer diameter of the bright ring = 0·70 mm.
Thickness „ „ = 0·18 mm.

When observed through a nicol there is a dark radial strip which rotates with the nicol but at twice its rate.

(*e*) Distance is negative and numerically not greater than about 10 cm. The appearances seen are exactly similar to those observed at an equal positive distance.

(*f*) When the source of light is brought near to the pin-hole the appearances seen are still the same, but all of them, except that of (*d*), have now a much less sharp outline.

(*g*) When the light incident on the pin-hole is plane polarized the ring seen in (*d*) is brightest at one radial strip, the brightness falling off on both sides until at the opposite point we have a dark strip.

(*h*) When the pin-hole is replaced by a slit of any shape, the phenomenon seen beyond about 10 cm. from the slit is a bright line of the same shape and size as the slit and surrounded by hazy light. Consequently we may call this phenomenon the image of the slit. It is erect and gets less and less bright as the distance of the screen on which it is obtained is increased. If the slit be illuminated with white light, this image is coloured with all the colours in the order in which they appear in a spectrum, and is something very much like the virtual image of a slit seen through a prism.

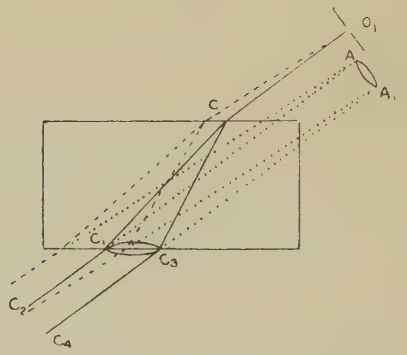
Before attempting an explanation of the above observations, we will first see why that advanced by Prof. Raman and Mr. Tamma does not appear to be quite adequate. They studied the phenomenon for distances mentioned in (*h*) above, and explained it in a more or less qualitative way as being a consequence of the external conical refraction exhibited by the crystal. Two arguments may be advanced against this view. In the first place, the phenomenon is observed under conditions when no external conical refraction could be exhibited, viz. when there is a very narrow cylindrical beam of incident light. Secondly, if this phenomenon were a consequence of the external conical refraction, the various appearances seen ought to be the same for the same distance from the second surface of the crystal. As we have seen above, this is not so. Hence the explanation seems to be incorrect.

Explanation of the formation of the ring described in (*d*).

Consider a small cone of rays issuing from a point O_1 of the pin-hole (fig. 1). Let O_1C be the ray that undergoes internal conical refraction. After emergence from the plate this ray will give rise to a circular cylindrical shell of light whose axis is parallel to O_1C. Take a ray C_1C_2 belonging to this cylinder of light. If we consider its neighbouring rays which belong to other rays of the initial cone of light coming out at O_1, it is clear that when these are produced backwards they will intersect very nearly at a point A on C_2C_1. If we now take into account all the emergent rays

we see that when they are produced backwards they will intersect in a ring of light AA_1 formed by internal conical

Fig. 1.



refraction. Since the pin-hole has a diameter 0·16 mm., the ring will have a thickness equal to 0·16 mm., its mean diameter being still the same as before. The observed thickness is 0·18 mm., showing a close agreement. The calculated diameter of the ring is 0·50 mm., while the observed mean diameter is 0·52 mm. The calculated value of the distance of the plane of the ring from the pin-hole is 6 mm., and this again agrees with the observed value which is 6 mm.

When the incident light is plane polarized it is easy to see that the ring formed is of the character described under (*g*) above.

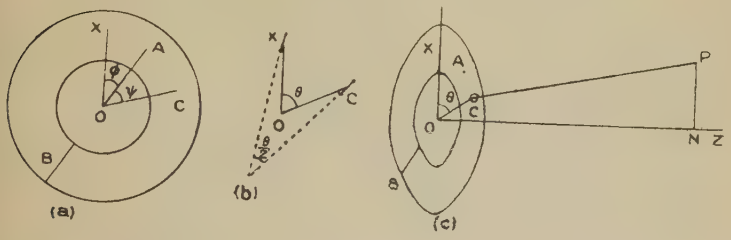
Explanation of the appearances seen.

We may now replace the pin-hole illuminated by plane polarized monochromatic light and the crystal, by the ring of light described under (*g*), and study the secondary effects produced by it. To simplify matters we shall suppose that the point-o-lite is a point source, and since the point-o-lite is a great distance from the pin-hole we may assume that the phase of vibration at any particular instant is the same all over the pin-hole, and consequently that it is also the same at all points of the ring.

Let ACB (fig. 2 below) be the ring of light with maximum brightness at one radial strip of it, the brightness gradually falling off on both sides until at the opposite strip B the illumination is zero. If $a \cos nt$ represent the vibration at A, it can be easily deduced that the vibration at C is given by $a \cos \frac{\psi}{2} \cos nt$, where $\psi = A\hat{O}C$. Each radial

strip consists of plane polarized light, the plane of polarization being different for different strips. If we pass from any point X on the ring to any other point C on it, then the line of vibration will be turned through half the angle through which the radius vector is turned when going from X to C (fig. 2 *b*). It is required to determine the illumination due to this ring at a point P in front of it.

Fig. 2.



Using cylindrical coordinates, take the axis of the ring as the Z axis. Draw PN⊥OZ. Take OX parallel to PN as the direction $\theta=0$. Denote $X\hat{O}A$ by ϕ.

Consider a small area dS at C whose coordinates are r, θ, 0. Let the coordinates of P be ζ, 0, b. Now

$$PC^2=b^2+r^2+\zeta^2-2r\zeta\cos\theta.$$

$$\therefore\quad PC=\xi=b+\frac{\zeta^2}{2b}+\frac{r^2-2r\zeta\cos\theta}{2b}$$ approx. since r and ζ are supposed to be very small compared with b. . . (I.)

Let the vibration at A be represented by $a\cos nt$.

Then that at C is given by $a\cos\frac{\phi-\theta}{2}\cos nt$.

∴ The vibration at P due to the secondary wavelets from the portion dS at C $=\frac{a}{\lambda\xi}\cos\frac{\phi-\theta}{2}\sin\left(\frac{2\pi\xi}{\lambda}-nt\right)d$S.

The direction of this vibration is inclined at an angle $\theta/2$ to that at the radial strip X. Resolving this vibration parallel and perpendicular to that at X we have:

the parallel component $=\frac{a}{\lambda\xi}\cos\frac{\phi-\theta}{2}\sin\left(\frac{2\pi\xi}{\lambda}-nt\right)\cos\frac{\theta}{2}\,d$S,

and the perpendicular component

$$=\frac{a}{\lambda\xi}\cos\frac{\phi-\theta}{2}\sin\left(\frac{2\pi\xi}{\lambda}-nt\right)\sin\frac{\theta}{2}.d\text{S}.$$

Summing up for the complete ring we get

the whole parallel component $$M=\int_{r_1}^{r_2}\int_0^{2\pi}\frac{a}{\lambda\xi}\cos\frac{\phi-\theta}{2}\times\sin\left(\frac{2\pi\xi}{\lambda}-nt\right)\cos\frac{\theta}{2}.\,r\,dr\,d\theta,$$

and

the whole perpendicular component $$N=\int_{r_1}^{r_2}\int_0^{2\pi}\frac{a}{\lambda\xi}\cos\frac{\phi-\theta}{2}\times\sin\left(\frac{2\pi\xi}{\lambda}-nt\right)\sin\frac{\theta}{2}.\,r\,dr\,d\theta, \quad . \quad . \quad \text{(II.)}$$

where r_1 and r_2 are the inner and the outer radii of the ring and $r\,dr\,d\theta$ has been written for dS.

On substitution of the value of ξ from (I.) we obtain

$$M=\frac{a}{\lambda}\int_{r_1}^{r_2}\int_0^{2\pi}\frac{1}{\xi}\cos\frac{\phi-\theta}{2}\sin\left\{\frac{2\pi}{\lambda}\left(b+\frac{\zeta^2}{2b}+\frac{r^2-2r\zeta\cos\theta}{2b}-nt\right)\right\}\times\cos\frac{\theta}{2}.\,r\,dr\,d\theta$$

$$=\frac{a}{\lambda b}\int_{r_1}^{r_2}\int_0^{2\pi}\cos\frac{\phi-\theta}{2}\sin(\alpha+\beta)\cos\frac{\theta}{2}.\,r\,dr\,d\theta, \quad . \quad \text{(III.)}$$

where b has been written for ξ in the denominator and

$$\alpha=\frac{2\pi}{\lambda}\left(b+\frac{\zeta^2}{2b}\right)-nt \quad \text{and} \quad \beta=\frac{\pi}{\lambda b}(r^2-2r\zeta\cos\theta).$$

(III.) can be written as

$$M=\frac{a}{\lambda b}(C_1\sin\alpha+S_1\cos\alpha), \quad . \quad . \quad . \quad \text{(IV.)}$$

where

$$C_1=\int_{r_1}^{r_2}\int_0^{2\pi}\cos\left[\frac{\pi}{\lambda b}(r^2-2r\zeta\cos\theta)\right]\cos\frac{\phi-\theta}{2}\cos\frac{\theta}{2}\,r\,dr\,d\theta$$

and

$$S_1=\int_{r_1}^{r_2}\int_0^{2\pi}\sin\left[\frac{\pi}{\lambda b}(r^2-2r\zeta\cos\theta)\right]\cos\frac{\phi-\theta}{2}\cos\frac{\theta}{2}\,r\,dr\,d\theta.$$

Similarly we can show that

$$N=\frac{a}{\lambda b}(C_2\sin\alpha+S_2\cos\alpha), \quad . \quad . \quad . \quad \text{(V.)}$$

where

$$C_2=\int_{r_1}^{r_2}\int_0^{2\pi}\cos\left[\frac{\pi}{\lambda b}(r^2-2r\zeta\cos\theta)\right]\cos\frac{\phi-\theta}{2}\sin\frac{\theta}{2}.\,r\,dr\,d\theta$$

and

$$S_2=\int_{r_1}^{r_2}\int_0^{2\pi}\sin\left[\frac{\pi}{\lambda b}(r^2-2r\zeta\cos\theta)\right]\cos\frac{\phi-\theta}{2}\sin\frac{\theta}{2}.\,r\,dr\,d\theta.$$

Therefore the intensity of illumination, I, at P

$$= \frac{a^2}{\lambda^2 b^2}(C_1^2 + C_2^2 + S_1^2 + S_2^2).$$

To evaluate the integrals C_1, S_1 . . . . , put

$$\frac{\pi r^2}{\lambda b} = \psi \quad \text{and} \quad \frac{2\pi r\zeta}{\lambda b} = x.$$

Then

$$C_1 = \int_{r_1}^{r_2} r dr \int_0^{2\pi} \left\{ \cos(\psi - x\cos\theta) \right\} \left\{ \cos\frac{\phi}{2}\cos^2\frac{\theta}{2} + \sin\frac{\phi}{2}\sin\frac{\theta}{2}\cos\frac{\theta}{2} \right\} d\theta$$

$$= \frac{1}{2}\int_{r_1}^{r_2} r dr \int_0^{2\pi} \left\{ \cos\psi\cos(x\cos\theta) + \sin\psi\sin(x\cos\theta) \right\} \times \left\{ \cos\frac{\phi}{2}(1+\cos\theta) + \sin\frac{\phi}{2}\sin\theta \right\} d\theta.$$

This reduces to

$$C_1 = \pi\cos\frac{\phi}{2}\left[\int_{r_1}^{r_2} r J_0(x)\cos\psi\, dr + \int_{r_1}^{r_2} r J_1(x)\sin\psi\, dr \right]$$

$$= \pi\cos\frac{\phi}{2}[\quad I_1 \quad + \quad I_2 \quad] \text{ say.}$$

Similarly we find that

$$S_1 = \pi\cos\frac{\phi}{2}(I_3 - I_4),$$

where

$$I_3 = \int_{r_1}^{r_2} r J_0(x)\sin\psi dr \quad \text{and} \quad I_4 = \int_{r_1}^{r_2} r J_1(x)\cos\psi\, dr.$$

In the same manner we obtain

$$C_2 = \pi\sin\frac{\phi}{2}(I_1 - I_2) \quad \text{and} \quad S_2 = \pi\sin\frac{\phi}{2}(I_3 + I_4).$$

$\therefore$ the intensity of illumination, I, at P

$$= \frac{a^2}{\lambda^2 b^2}(C_1^2 + S_1^2 + C_2^2 + S^2_2)$$

$$= \frac{a^2}{\lambda^2 b^2}(I_1^2 + I_2^2 + I_3^2 + I_4^2 + 2[I_1 I_2 - I_3 I_4]\cos\phi).$$

This is the illumination at P when the incident light is plane polarized. If the incident light be unpolarized, we may assume that it is plane polarized light whose azimuth is

changing very frequently. In this case the above equation becomes

$$I \propto (I_1^2 + I_2^2 + I_3^2 + I_4^2)$$

since the mean value of $\cos\phi$ is zero.

We supposed at the beginning that the point-o-lite was a point source. In reality it subtends a small angle χ at the pin-hole. In this case the illumination at P is the average of I taken over a circle with P as centre and diameter $b\chi$. In practice, after obtaining the value of I for different distances ζ of P from the axis OZ, the illumination at any distance ζ can be determined graphically.

Evaluation of the integrals I_1, I_2, *etc.*

Change the variable to x and we have

$$I_1 = \left(\frac{\lambda b}{2\pi\zeta}\right)^2 \left[\int_0^{x_2} x J_0 \cos\psi dx - \int_0^{x_1} x J_0 \cos\psi dx\right],$$

where J_0 stands for $J_0(x)$ and ψ, now expressed as a function of x, is equal to $\frac{\lambda b}{4\pi\zeta^2}x^2$.

These can be easily integrated by parts. (See Gray and Mathew's Treatise on Bessel Functions, 1895, p. 168.)

Introducing the Lommel series "U" we define

$$U_{1,m} = \frac{y_m}{x_m} J_1(x_m) - \left(\frac{y_m}{x_m}\right)^3 J_3(x_m) + \left(\frac{y_m}{x_m}\right)^5 J_5(x_m) - + \ldots.$$

and

$$U_{2,m} = \left(\frac{y_m}{x_m}\right)^2 J_2(x_m) - \left(\frac{y_m}{x_m}\right)^4 J_4(x_m) + \left(\frac{y_m}{x_m}\right)^6 J_6(x_m) - + \ldots.$$

Then

$$I_1 = \frac{\lambda b}{2\pi}\left[\cos\psi_2 \cdot U_{1,2} + \sin\psi_2 \cdot U_{2,2} - \cos\psi_1 \cdot U_{1,1} - \sin\psi_1 \cdot U_{2,1}\right],$$

in which $y_1 = 2\psi_1$ and $y_2 = 2\psi_2$, ψ_1 and ψ_2 being the values of ψ when x has the values x_1 and x_2 respectively.

We can get a similar series for I_3.

These series are convergent when $\frac{y_2}{x_2}$ and $\frac{y_1}{x_1}$ arc <1. If one or both of them be greater than 1 we can integrate I_1

by parts in reverse order and get the corresponding "V" series.

$$I_2=\int_{r_1}^{r_2} rJ_1(x)\sin\psi dr$$

$$=\left(\frac{\lambda b}{2\pi\zeta}\right)^2\left[\int_0^{x_2} xJ_1\sin\psi dx-\int_0^{x_1} xJ_1\sin\psi dx\right]$$

where $J_1=J_1(x)$.

Now,

$$\int_0^x xJ_1\sin\psi dx=\int_0^x x^2J_1\cdot\frac{\sin\psi}{x}dx$$

$$=x^2J_2\cdot\frac{\sin\psi}{x}-\int_0^x x^3J_2\cdot\frac{d}{xdx}\left(\frac{\sin\psi}{x}\right)dx$$

$$=x^2J_2\cdot\frac{\sin\psi}{x}-x^3J_3\frac{d}{xdx}\left(\sin\frac{\psi}{x}\right)$$

$$+\int_0^x x^4J_3\frac{d}{xdx}\cdot\frac{d}{xdx}\left(\frac{\sin\psi}{x}\right)dx,$$

$$=x^2J_2\cdot\frac{\sin\psi}{x}-x^3J_3\frac{d}{xdx}\left(\frac{\sin\psi}{x}\right)$$

$$+x^4J_4\left(\frac{d}{xdx}\right)^2\frac{\sin\psi}{x}-+\ .$$

Let $\psi=\frac{1}{2}\kappa x^2$; then $\frac{d\psi}{\kappa}=x\,.\,dx$ and $x=\sqrt{\frac{2}{\kappa}}\cdot\sqrt{\psi}$. We now have

$$\int_0^x xJ_1\sin\psi\,dx=\sqrt{\frac{\kappa}{2}}\left\{x^2J_2\cdot\frac{\sin\psi}{\sqrt{\psi}}-x^3J_3\cdot\kappa\frac{d}{d\psi}\left(\frac{\sin\psi}{\sqrt{\psi}}\right)\right.$$

$$\left.+x^4J_4\cdot\kappa^2\frac{d^2}{d\psi^2}\left(\frac{\sin\psi}{\sqrt{\psi}}\right)-+\ldots\right\}$$

$$=\frac{x}{\sqrt{2\kappa}}\left\{\kappa xJ_2\cdot\frac{\sin\psi}{\sqrt{\psi}}-\kappa^2x^2J_3\frac{d}{d\psi}\left(\frac{\sin\psi}{\sqrt{\psi}}\right)\right.$$

$$\left.+\kappa^3x^3J_4\frac{d^2}{d\psi^2}\left(\frac{\sin\psi}{\sqrt{\psi}}\right)-+\ldots\right\}$$

$$=\frac{x}{\sqrt{2\kappa}}\left\{\frac{y}{x}J_2\frac{\sin\psi}{\sqrt{\psi}}-\frac{y^2}{x^2}J_3\frac{d}{d\psi}\left(\frac{\sin\psi}{\sqrt{\psi}}\right)\right.$$

$$\left.+\frac{y^3}{x^3}J_4\frac{d^2}{d\psi^2}\left(\frac{\sin\psi}{\sqrt{\psi}}\right)-+\ldots\right\}$$

in which $y=\kappa x^2$.

It can be easily proved that this series is convergent when $\frac{y}{x} \leqslant 1$. When $\frac{y}{x} > 1$ the evaluation of I_2 is somewhat more tedious. But in the actual problem the maximum value of $\frac{y}{x}$ used was 1·2 for which the series was still sufficiently convergent. If we now introduce the series

$$A_m = \left(\frac{\lambda b}{2\pi\zeta}\right)^2 \cdot \frac{x^m}{\sqrt{2\kappa}} \left\{ \frac{y_m}{x_m} J_2(x_m) \frac{\sin\psi_m}{\sqrt{\psi_m}} - \left(\frac{y_m}{x_m}\right)^2 J_3(x_m) \left[\frac{d}{d\psi}\left(\frac{\sin\psi}{\sqrt{\psi}}\right)\right]_m + - \ldots \right\}$$

where $\left[\frac{d^s}{d\psi^s}\left(\frac{\sin\psi}{\sqrt{\psi}}\right)\right]_m$ means that after the differentiation of $\frac{\sin\psi}{\sqrt{\psi}}$ s times with respect to ψ, ψ_m is to be written for ψ in the result; y_m and ψ_m are the values of y and ψ respectively when $x = x_m$, we obtain

$$I_2 = A_2 - A_1.$$

In a similar manner we can show that

$$I_4 = B_2 - B_1,$$

where B_m is obtained from A_m by substituting $\cos\psi$ for $\sin\psi$.

A numerical calculation when the distance of P was 10·4 cm. from the plane of the ring was carried out for different distances of P from the axis. To facilitate computation it was assumed that the thickness of the ring was equal to half the outer radius of the ring. (Actually the thickness of the ring was 0·18 mm. and the outer radius was 0·35 mm.)

	calc.	obs.
Outer diameter of the inner ring	= 0·35 mm.	0·30 mm.
,, ,, outer ,,	= 0·80 mm.	0·85 mm.
Diameter of the spot	= 0·10 mm.	0·13 mm.

The agreement is suprisingly close when we consider the approximations we have made.

Referring to the value of I, we see that for a given value of b, the value of I varies with ζ only. Hence on a given plane PN the illumination will be the same at all points on the circumference of a circle which has its centre at N (fig. 2). This shows that the various appearances seen at the plane PN will be either concentric rings or a disk. This is the reason why only concentric rings and a disk were seen at different distances of the focussed plane from the plane of the internal conical refraction ring.

We can now understand the formation of the continuous image of a slit of any form by the crystal plate. In the case of a pin-hole, the concentration of light along the axis of the internal cone of light is in the form of a small spot. Now a slit can be supposed to be formed of pin-holes one near the other, so that on this side of the crystal the spots will be arranged exactly in the same manner, in other words we shall have an image of the slit which is continuous, erect, and of unit magnification. If the slit be illuminated with light which shows a line spectrum, *e. g.*, the light from a mercury arc, it is not difficult to infer that there will be an image corresponding to each line in the light, since each line will have its own cylinder of light formed by internal conical refraction.

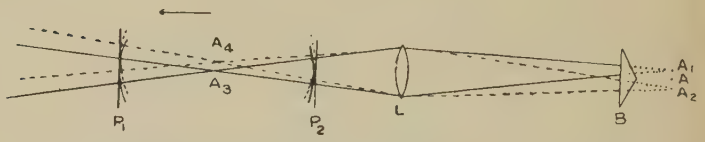
With the pin-hole as the source of light, if the point-o-lite be brought near it, it follows that the phase of vibration at any instant will not be the same at all points of the pin-hole, and consequently it will not be uniform over the luminous ring. As a result of this we ought to expect a diminution in the sharpness of the secondary phenomena observed. This corresponds exactly to what is described under (*f*) above.

One other observation that remains to be explained is that described under (*e*), namely, that the appearances seen on one side of the ring are the same as those seen on the other side at an equal distance. This observation gets a ready explanation from a similar observation made accidentally by me a few years back.

Images A_3 and A_4 (fig. 3) are obtained with the lens L of the two virtual images A_1 and A_2 which are formed by the bi-prism B of a fine slit A illuminated with sodium light. The distances between the bands formed on a plane P_1 on one side of A_3A_4 are measured. When the micrometer eyepiece is moved so that the plane of its cross-wires coincides with

P_2 at an equal distance from A_3A_4 and on the other side of it, bands are observed whose distance apart is found to be the same as the previous one.

Fig. 3.



An explanation of this may be given in the following way. The bands on the plane P_1 are due to the interference between cylindrical waves of light starting from A_3 and A_4 and moving in the direction of the arrow. Now if all the velocities be reversed, *i. e.*, if the expanding cylinders of light be made to contract, we must still see the same bands but now from the opposite direction. This is exactly what we have at the plane P_2. In a similar manner we can explain the observations recorded in (*e*).

One other experiment was performed to test our explanation. A mercury arc lamp was used as the source of light. To facilitate measurements a slit was substituted for the pinhole. When the crystal was oriented so as to produce the Raman-Tamma image of the slit, two images were obtained corresponding to the two brightest lines in the arc, the green 5461 Å.U. line and the violet 4358 Å.U. line. These two images were surrounded by hazy light and were viewed through a Gaussian eyepiece.

The linear separation between the two images was measured by the micrometer scale in the eyepiece. During the measurement it was found advisable to suppress each of these images in turn by means of a suitable filter. The crystal was then rotated about the direction of propagation of light until the separation was a maximum. This meant that the plane containing the axes of the two cylindrical shells of green and violet light for any ray formed by internal conical refraction was perpendicular to the slit. Measurements of the separation for different distances between the slit, the scale, and the crystal showed that the separation is proportional to the distance between the slit and the scale and is independent of the position of the crystal between them. This is as it should be.

From these measurements was obtained the angle between the optic axes for the green and the violet light used above. It was $11' \pm 1'{\cdot}5$. The calculated value was $11'{\cdot}5$.

In conclusion I gratefully wish to put on record my thanks to Prof. A. W. Porter, D.Sc., F.R.S., not only for having suggested to me the above piece of work, but also for having given me great encouragement while the above experiments were being carried out at the Physical Laboratory of University College, London.

CXXXIX. *Notices respecting New Books.*

Astronomical Physics. By F. J. M. Stratton, D.S.O., M.A., F.Inst.P. [Pp. xi+213 with 32 plates.] (London: Methuen & Co., Ltd., 1925. Price 12*s.* 6*d.* net.)

THIS book contains, in comparatively small compass, an excellent summary of the main facts of astronomical physics and of their theoretical interpretation. In his preface, the author states that "His aim has been to provide a useful book on the subject for the student, and one which every astrophysicist and not a few spectroscopists would want constantly within reach." It cannot be doubted that he has been successful in this aim, and workers in this subject will be grateful for the detailed references to original papers given throughout and for the useful series of tables at the end, containing data compiled from a number of different sources. The number of references in the footnotes bearing the dates 1924 or 1925 is an indication that recent work, right up to the time of passing the volume through the press, has been incorporated.

After a brief historical introduction and an account of instruments and laboratory investigations, the sun and solar system are dealt with, insofar as spectroscopic methods can give information about them. A chapter on stellar radiation follows, including a brief account of Eddington's recent work. The next chapters on line of sight motion and stellar classification contain a mine of information for reference purposes. Succeeding chapters deal with giant and dwarf stars, nebulæ, novæ, variable stars, stars with peculiar spectra, and finally a chapter on speculations in cosmogony.

The volume is written from the point of view of the practical astrophysicist rather than of the theorist. But for the latter a few stars of abnormal behaviour may provide the key for solving some of the riddles of the Universe. The volume contains an account both of the normal and of the abnormal, and workers in both fields cannot fail to find it of very great value in their investigations.

Elements of the Mathematical Theory of Limits. By J. G. Leathem, Sc.D. [Pp. viii+288.] (London: G. Bell & Sons, Ltd., 1925. Price 14*s.* net.)

This book was written in the belief that the earlier in a course of mathematical studies precise and logical ideas are introduced, the better it is for the student. It therefore demands no greater mathematical knowledge on the part of the reader than the binomial theorem for an integral exponent, the meaning of logarithms, the elements of trigonometry and a small amount of geometry. Its study may be commenced at a very early stage and it might well form an introduction to such a volume as Hardy's 'Pure Mathematics.' The student who has grasped the ideas in this book will be well equipped to commence the study of the infinitesimal calculus and the theory of infinite series. The treatment is very elementary and clear and the more difficult points are very carefully and fully dealt with and occasionally postponed to a later stage, *e. g.* "The continuity of some familiar functions will be discussed later. For the present the student may take it that, for all but special exceptional values of the independent variable, all algebraic functions and other functions commonly employed in elementary mathematics are continuous." The book does not introduce double limits, and such matters as the theory of double series and uniform convergence are left for a later stage in the student's training. An excellent series of examples is included.

It is sad to recall that the author died soon after the completion of his manuscript and two friends have supervised its printing. The manuscript has been followed without alteration, save for the correction of obvious slips and the removal of occasional obscurities.

The Principles of Sound Signalling. By Morris D. Hart, M.Sc., and W. Whately Smith, M.Sc. (Constable & Co., 1925.)

This book supplies a want. It contains an account of recent advances in methods of generating sound signals and of experimental methods of arriving at quantitative estimates of their efficiency. The subject is bristling with difficulties. The strength of the source and the intensity of sound derived therefrom at varying distances have to be measured. The authors, quoting from a paper by one of them appearing in the 'Proceedings of the Royal Society,' advocate the use of the hot-wire microphone in measuring the intensity of the sound. These measurements, although made upon a small scale, support known experimental data respecting the heavy loss attending sound propagation in the atmosphere.

The discussion in Chapter IV. on the effects of meteorological conditions on sound transmission is clear and to the point. Chapters V. and VI. contain a review of the principal instrumental

methods producing sound signals of long range; which review closes in favour of the Centrifugal Siren.

A valuable Appendix discusses methods of measuring acoustical energy. The authors ask if it would not be practicable to adopt a system of empirical units and standards for acoustical work pending the development of the technique necessary for the determination of sound in absolute units. A suggestion which is amply justified, as everyone concerned in the administration of lighthouse funds is aware.

The book is clearly and tersely written. It will be of value to all those who have dealings with problems of coastal navigation or, more generally, with sound signalling.

CXL. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 1180.]

March 25th, 1925.—Dr. J. W. Evans, C.B.E., F.R.S., President, in the Chair.

THE following communications were read:—

1. 'On the Clay Pebble-Bed of Ancon (Ecuador)'. By Charles Barrington Brown, M.C., M.A., F.G.S., and Robert Ashley Baldry, B.A., F.G.S.

This paper gives an account of a peculiar clay pebble-bed, varying in thickness from 550 to 900 feet, which crops out on the southern shore of the Santa Elena Peninsula, at the northern extremity of the Gulf of Guayaquil (Ecuador). It consists of polished, rounded, or subrounded pebbles of harder clay, embedded in a matrix of softer clay; the pebbles vary from the size of a pin's-head up to 2 or 3 inches in diameter. In addition, it contains large and partly rounded boulders of sandstone, foraminiferal limestone, grit, polished quartz-pebbles, etc., and in some cases masses of limestone occur many cubic yards in bulk. The upper limit of the bed is usually well-defined, and has subsequently been faulted and folded with the overlying strata. The lower limit is never seen in the sea-cliffs, but has been proved by boring. It is considered by the authors to be the result of a great post-Oligocene overthrust in soft sands and clays of Tertiary age. The direction of thrusting is from the east-south-east (the Brazilian over the Pacific block). The occurrence is thought to give an insight into the mechanism of overthrusting in soft strata, and to illustrate the formation, by this means, of a thick stratum difficult to differentiate from a stratigraphical unit or a boulder-clay.

2. 'The Pre-Cambrian Volcanic Rocks of the Malvern Inlier.' By John Isaac Platt, M.Sc., F.G.S.

The region described occurs about the central part of the Malvern Range, and consists largely of volcanic rocks. Although the area has received considerable attention at the hands of earlier investigators, the volcanic rocks have not been described of recent years. These rocks are of Pre-Cambrian age, and belong to a distinctly sodic suite comprising soda-rhyolites, keratophyres, and spilites.

The rhyolites possess a ground-mass which shows a micrographic structure, and represents the eutectic mixture of the constituent minerals: namely, quartz and felspar (chiefly albite). In many of the types phenocrysts of these two minerals occur. The rhyolites, as well as the majority of the other rocks, contain epidote in varying amounts. Chlorite sometimes occurs with the epidote and the association of these two minerals suggests simultaneous formation, while further there is evidence of a change of some of the chlorite into epidote.

The keratophyres contain lath-shaped albite-crystals and much magnetite, and show trachytic structure. Mafic minerals are markedly absent, but chlorite and epidote are well represented. There are several interesting variations of this type.

The more basic lavas, the spilites, are usually vesicular. No pillow-structure was seen. Here again soda-rich felspars occur, but they are frequently in the form of microlites, which are so arranged as to give a variolitic structure to the rock. Secondary chlorite and epidote are also present.

There are a few pyroclastic rocks developed. Although those examined were of an acid composition, there can be little doubt that more basic types also occur.

A number of minor intrusions have been injected into the lavas. In the south-west of the area described two dykes of a comparatively fresh ophitic dolerite crop out, while a subophitic variety of the same type is found in the north-west. There are several dykes and a volcanic neck of epidiorite in the east of the area, This epidiorite appears to be an uralitized modification of the coarse ophitic dolerite. In some varieties of this rock the secondary changes have been so great as to produce an epidote-uralite-rock.

As the boundaries of the series are all faulted ones, the Pre-Cambrian age can only be determined by indirect means.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

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